

EXHIBIT 12

Novel Resist Systems for EUV Lithography: LER, Nanoparticle, Chain-Scission and MORE

I. Introduction.

II. Chain-Scission Polymers:
Polyesters, Polyethers and
Polyalkynes.

III. Molecular Organometallic
Resists for EUV(MORE).

IV. Summary.

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5/20/2013

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Dr. Daniel Freedman

Dr. John Welch

*Submitted in partial fulfillment of the degree of Doctor of Philosophy in Nanoscale
Science at the College of Nanoscale Science and Engineering, University at Albany*

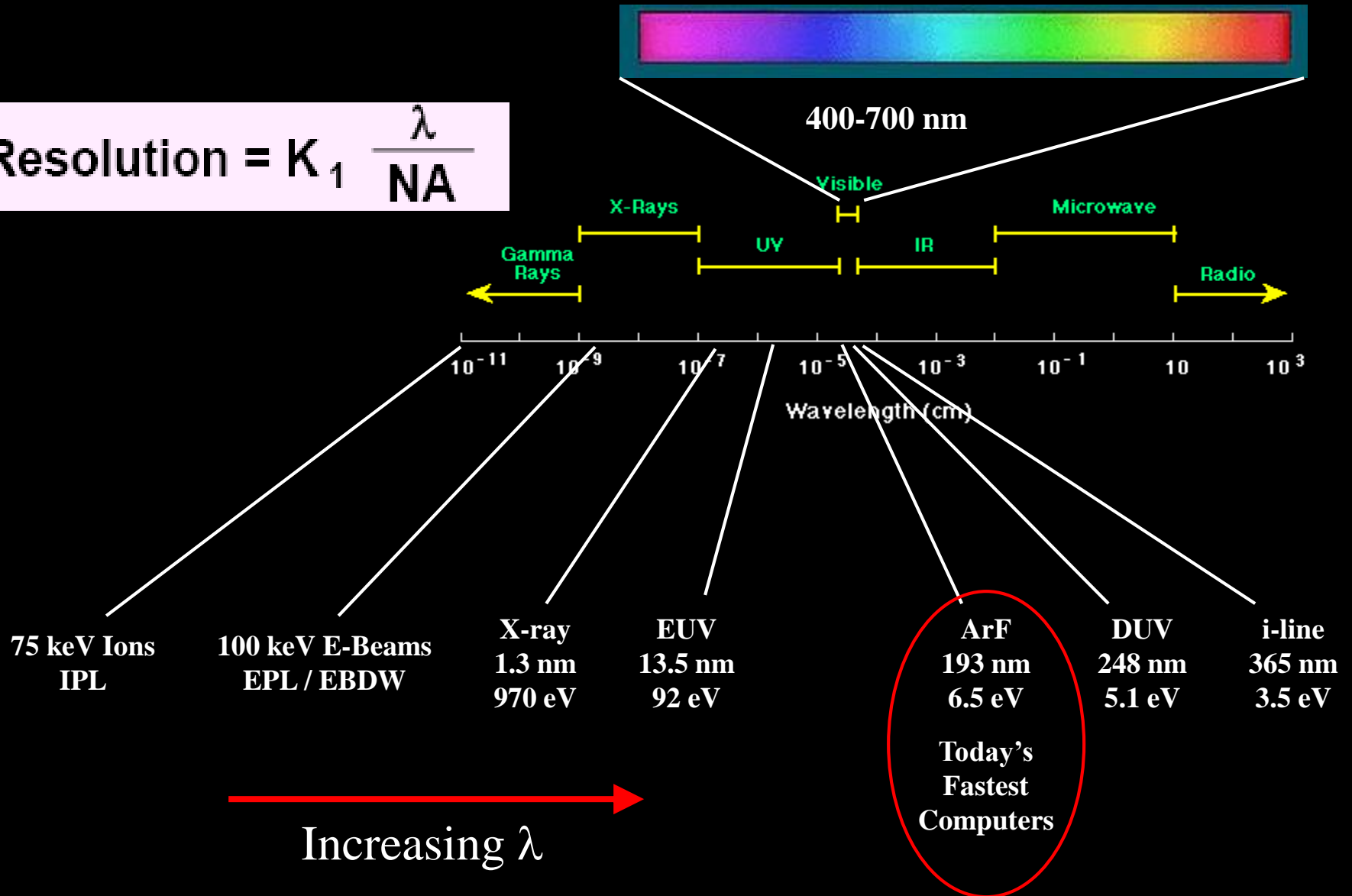
EUV = Extreme Ultraviolet

LER = Line-Edge Roughness

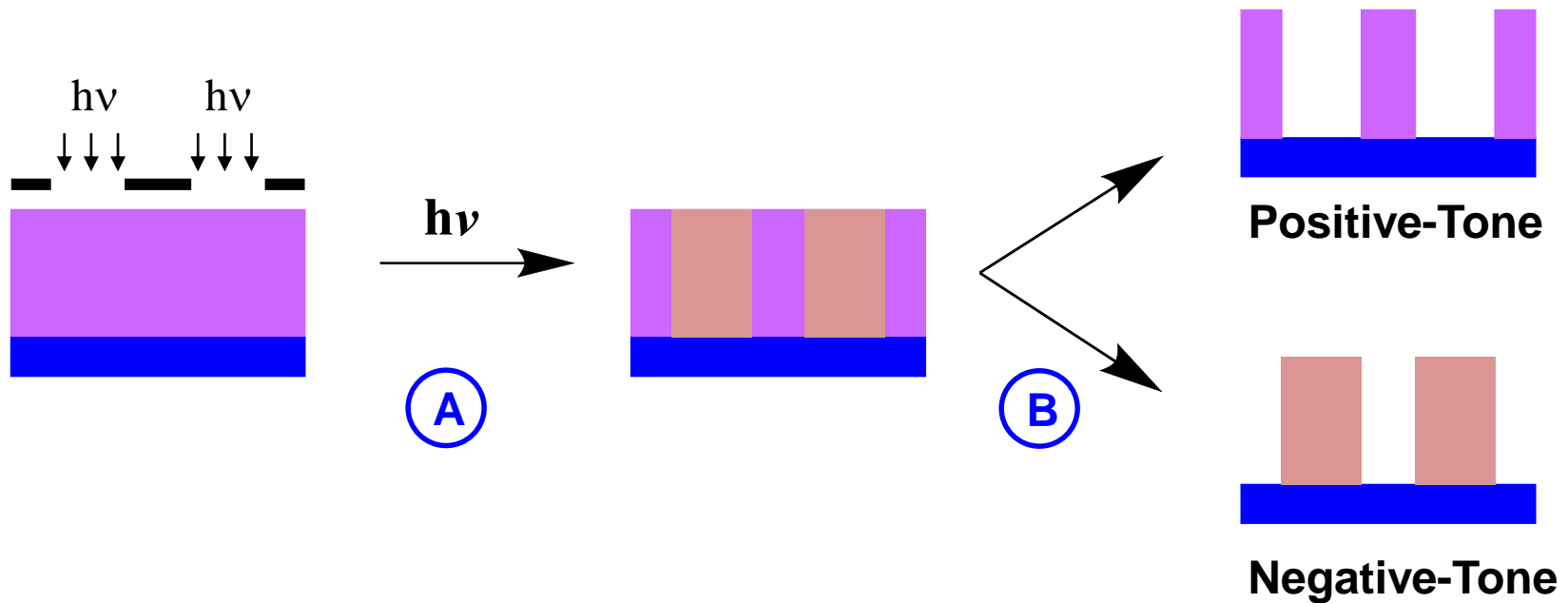
MORE = Molecular Organometallic Resists for EUV

I. What is Extreme Ultraviolet (EUV)?

$$\text{Resolution} = K_1 \frac{\lambda}{\text{NA}}$$



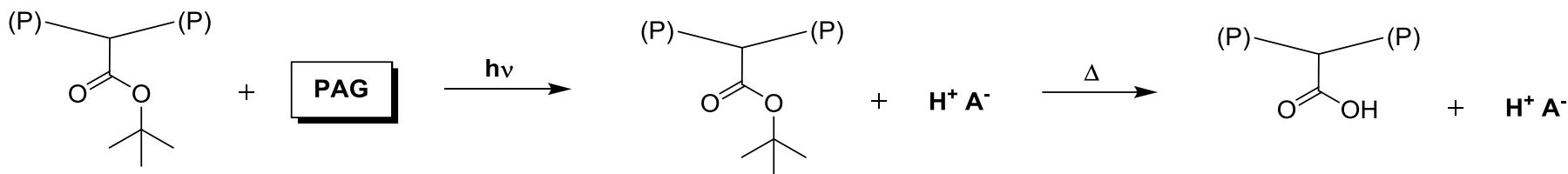
Basic Photoresist Process



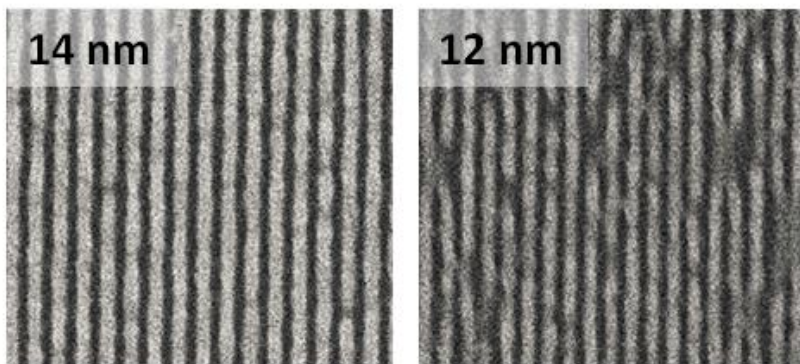
- (A) Exposure** – Resist is exposed through a mask, creating a chemical change where the light hits the film (may or may not include a post-exposure bake (PEB)).
- (B) Develop** – Film is washed in a developer/solvent that is selective to the chemical change which occurred during exposure.

Organic Chemically-Amplified Photoresists

Today, most EUV photoresists are chemically amplified. The acid-sensitive resist polymer is combined with a photoacid generator (PAG). Upon exposure, the PAG generates photoacid which catalyzes the polymer decomposition.



JSR Micro resist imaged for 14 and 12 nm h/p lines at a dose of 15 mJ/cm².

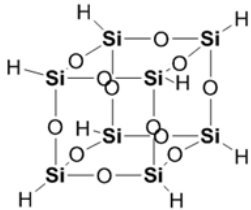


The high sensitivities of catalysis plus careful engineering have led to powerful resist systems.

Recent Advances in Inorganic Photoresists

Recently, some researchers have abandoned organic resist designs and have developed several new inorganic resists with excellent potential.

HSQ



7-nm h/p lines
294 mJ/cm²

Hafnium-Oxide Nanoparticles

Inpria

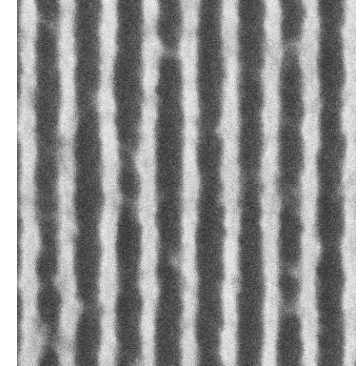


12-nm h/p lines
25 mJ/cm²



8-nm h/p lines
47 mJ/cm²

Cornell



36-nm h/p lines
12 mJ/cm²

Thesis Questions

Novel resist design is needed to improve resist performance.

Hypothesis 1: Acid-cleavable chain-scission polymers can be made that function as resists.

- Can acid-cleavable polymers be made and how do they function as resists?
- How do the mechanical and physical properties of the polymer affect the lithographic performance of these chain-scission resists?
- Can high T_g, hydrophilic resist polymers be made using the palladium catalyzed Hiyama coupling reaction?

Hypothesis 2: Molecular-inorganic resists can be made for EUV from high optical-density materials.

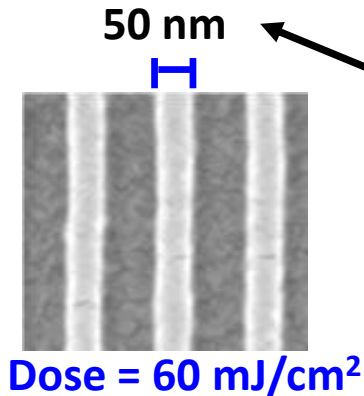
- Can inorganic/organometallic compounds act as photoresists?
- How does ligand structure affect performance?
- How do different metals affect performance?

EUV Resist Goals: Beat the RLS Tradeoff

EUV resists need to improve Resolution, LER and Sensitivity.

It has been found difficult to improve all three of these properties simultaneously.

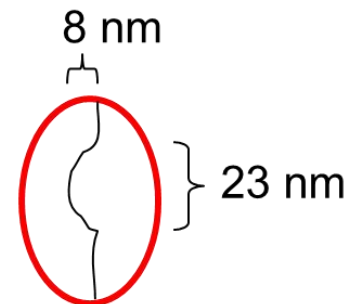
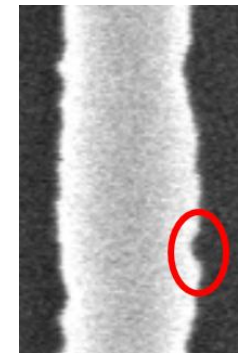
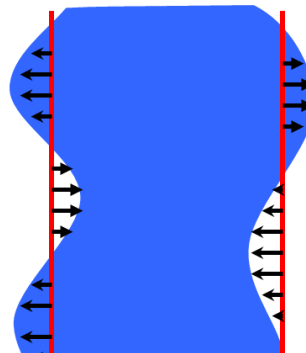
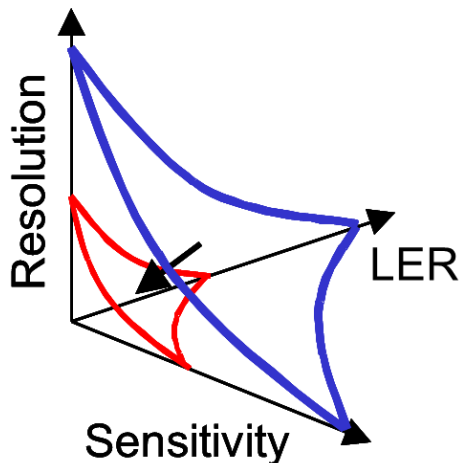
This is known as the RLS tradeoff.



Resolution – Size of Pattern

Sensitivity – Dose required to expose pattern

Line Edge Roughness (LER) – Amount a printed line deviates from a perfect line



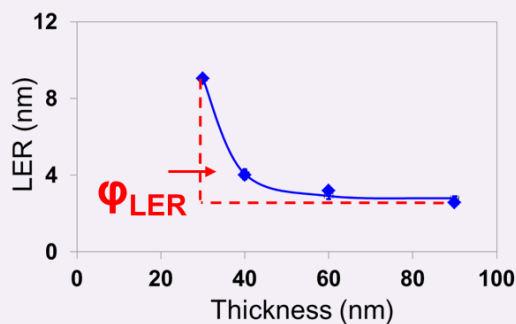
Case 1:24-cv-0120-LKS-RCL Document 2-1 Filed 01/31/24 Page 30 of 34

Novel Resist Systems for EUV Lithography: LER, Nanoparticle, Chain-Scission and MORE

Physical
Chemistry:

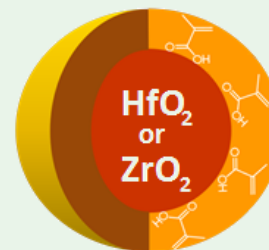
Organic:

LER Degradation



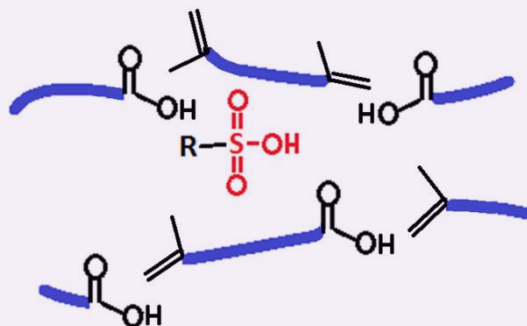
Inorganic:

Ligand Design for Hafnium Nanoparticle Resists

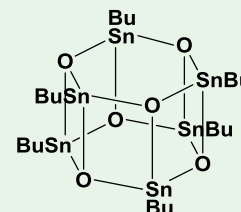


Synthetic
Chemistry:

Chain Scission Polymers



Molecular Organometallic Resists for EUV (MORE)



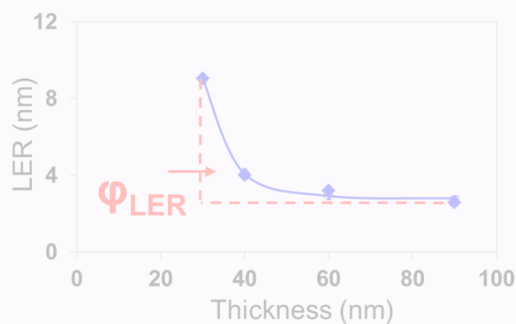
Novel Resist Systems for EUV Lithography: LER, Nanoparticle, Chain-Scission and MORE

Physical
Chemistry:

Synthetic
Chemistry:

Organic:

LER Degradation

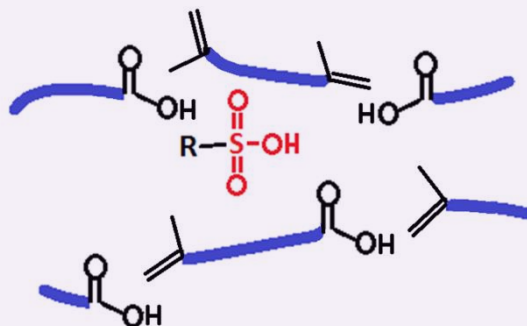


Inorganic:

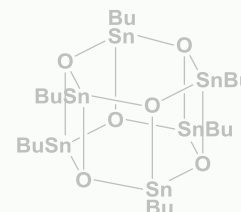
Ligand Design for Hafnium Nanoparticle Resists



Chain Scission Polymers

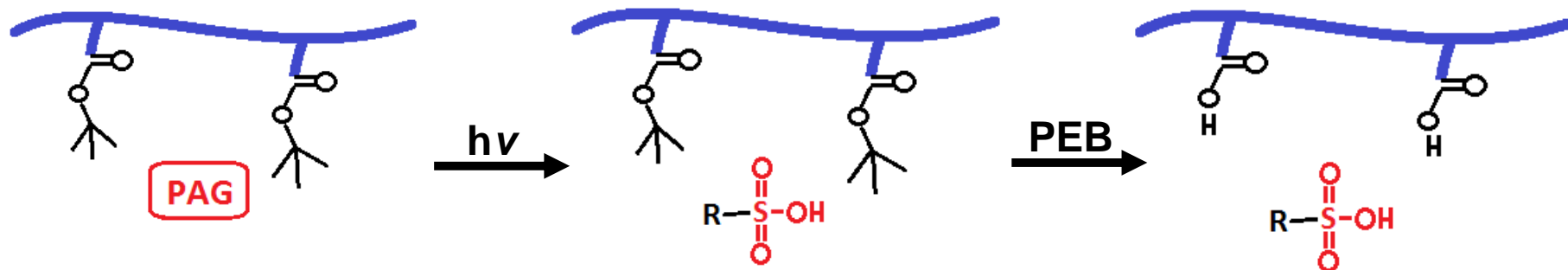


Molecular Organometallic Resists for EUV (MORE)

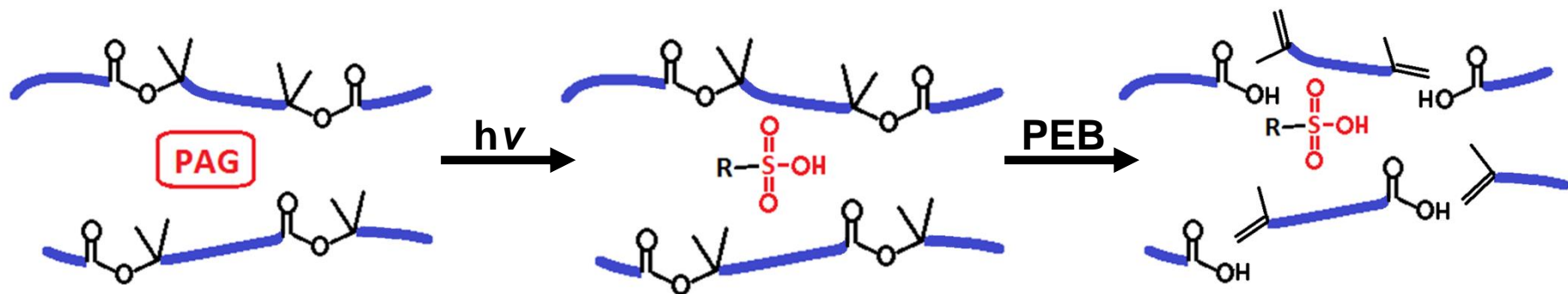


II. Chain-Scission Polymers: Polyesters, Polyethers and Polyalkynes

Traditional Chemically Amplified Resist:



Chain-Scission Polymer :

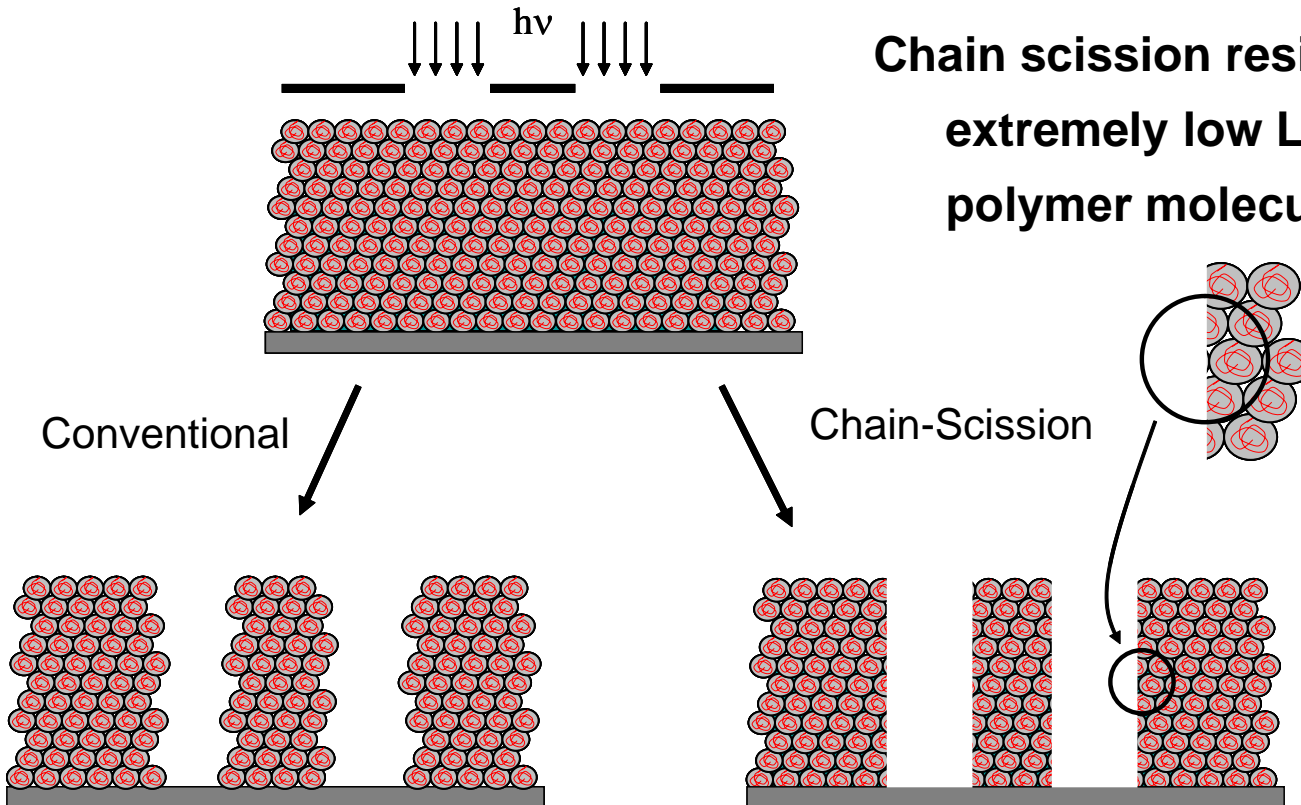


Proposed Advantages.

Lower LER Due to the Scission of Polymers

The chain scission reaction is similar to PMMA resists.

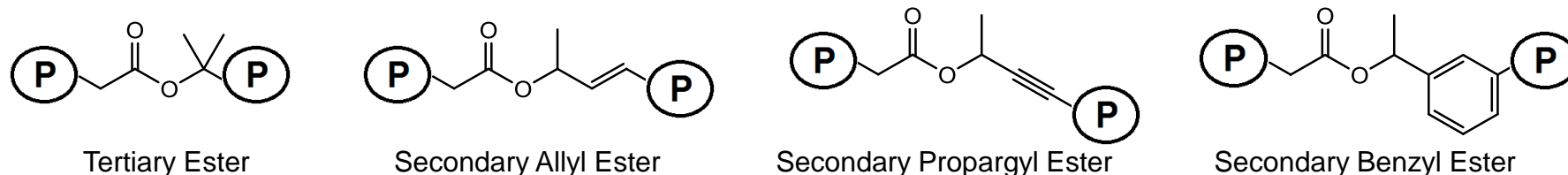
Chain scission resists could have extremely low LER because the polymer molecules are “cut through”



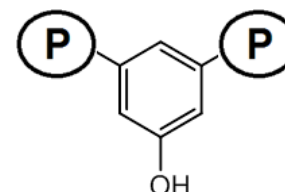
Cleavable Polymers Design Criteria:



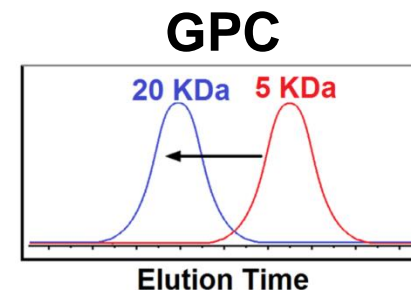
1. Acid cleavable groups in the backbone:



2. Control of dissolution properties:



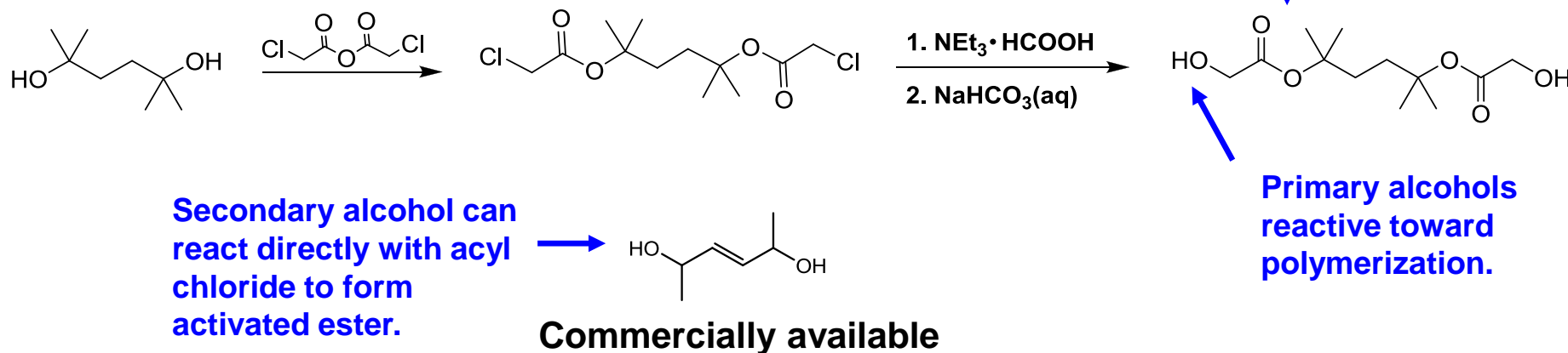
3. Control of molecular weight during polymerization:



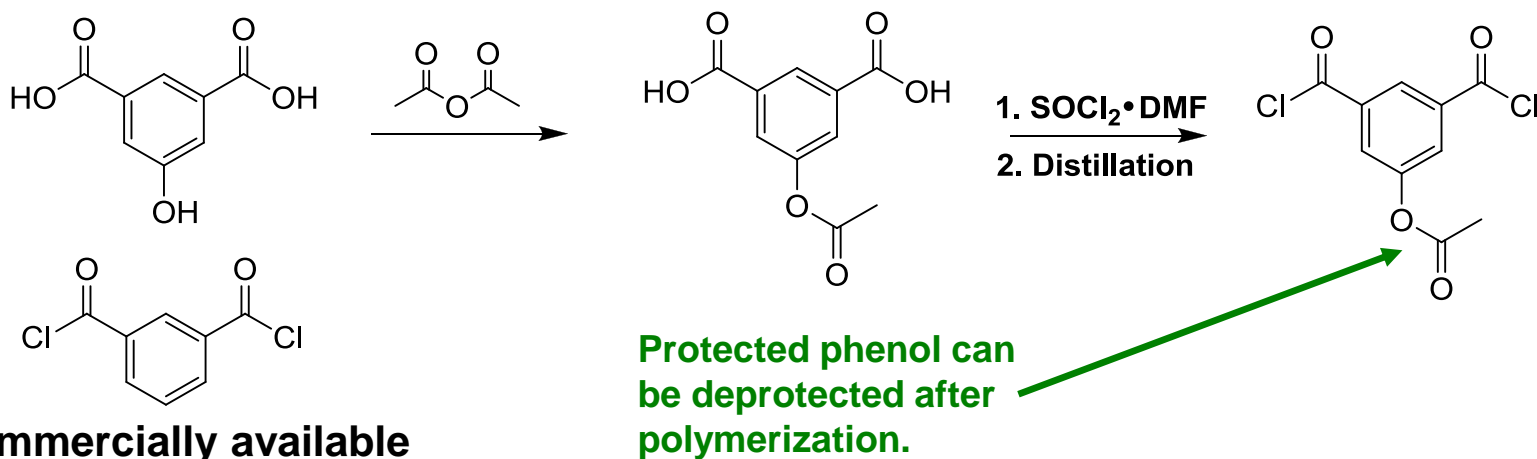
(P) = Polymer

Generation I – Polyesters: Monomer Synthesis

Acid-Cleavable Diols -

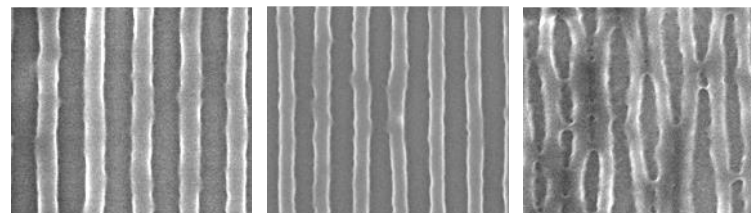


Di (Acid Chloride) Linkers -



Case 1:24-cv-00120-BKS-ML Document 24-35 Filed 01/31/24 Page 15 of 64

Generation I – Lithographic Results

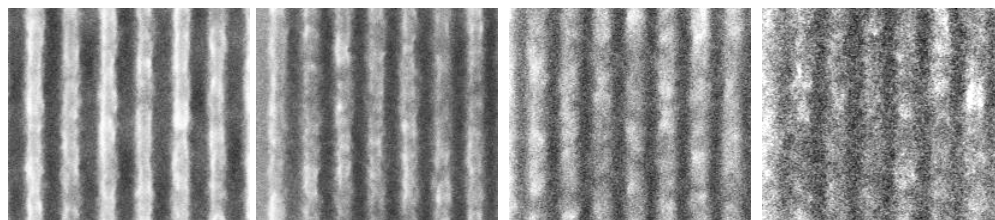


100 nm

80 nm

60 nm

Dose = 6.9 mJ/cm² at 70 °C PEB



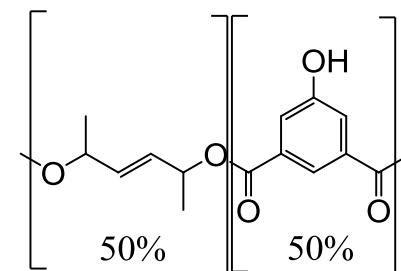
50 nm

45 nm

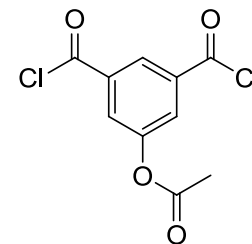
40 nm

36 nm

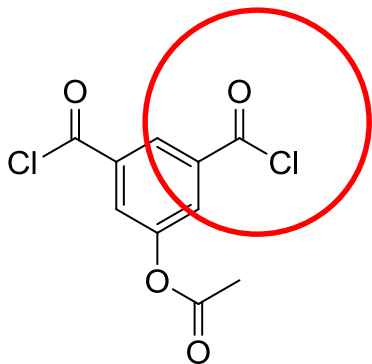
Dose = 22.5 mJ/cm² at 110 °C PEB



Although hopeful results were achieved, large variations in performance were observed. We hypothesize this is linked to impurities in the di(acid chloride) linkers.

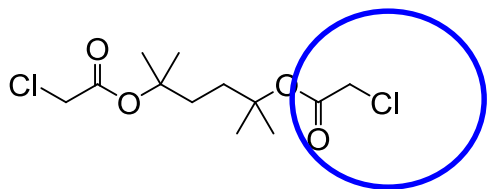


Generation II – Polyethers: a More Stable System



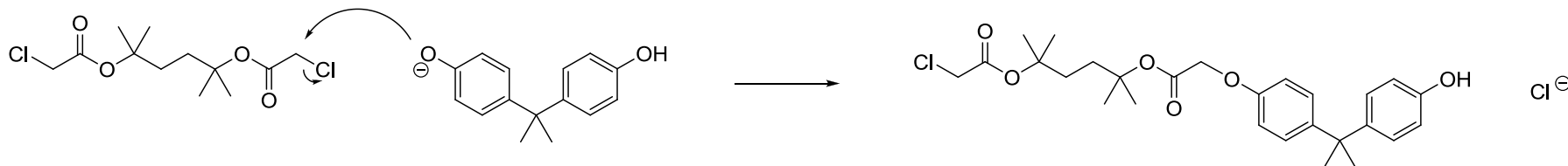
Generation I: Acid chlorides react with water, react with amine bases and thermally decarboxylate.

Impurities in this group will limit polymer Mw and altered mechanical properties.

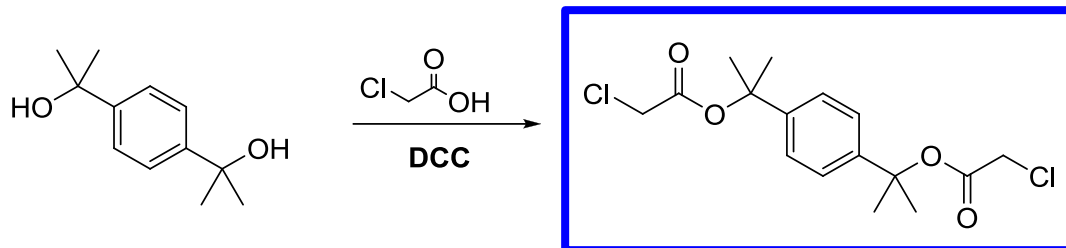
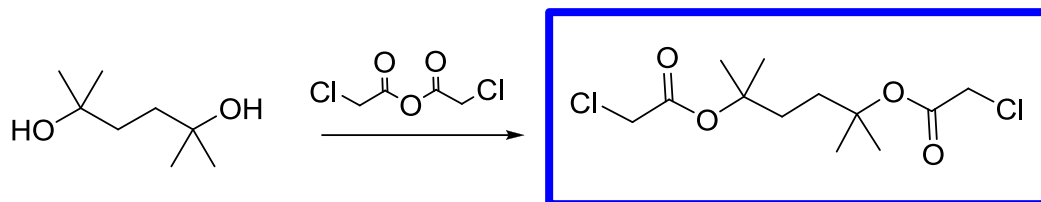


Generation II: α -Chloro esters are reactive enough to form polymers, but not reactive enough to form side products.

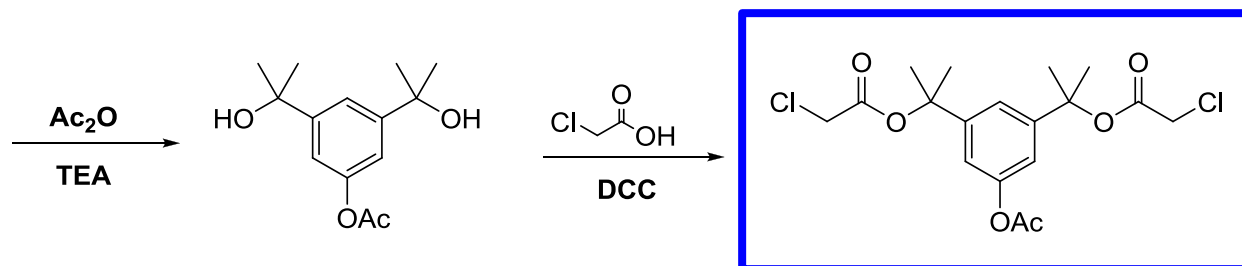
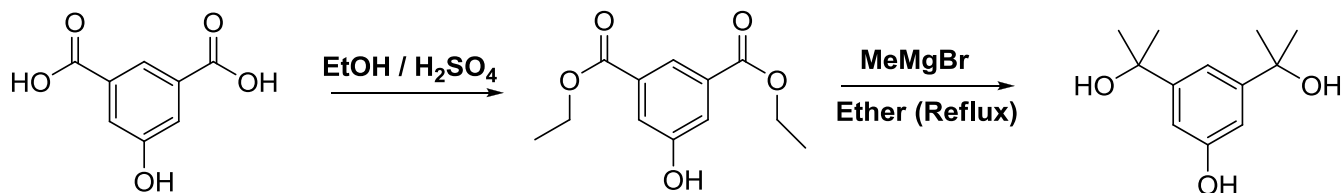
Polyether Condensation:



Generation II – Monomer Synthesis



**Lower Activation
Cleavable Group**



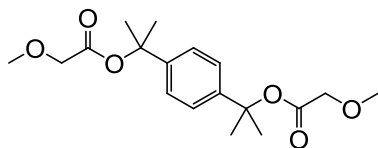
**Lower Activation and
Increased Solubility from
Phenol**

Steglich et al., Angew. Chem. Int. Ed., 17, pp. 522-24, 1978.

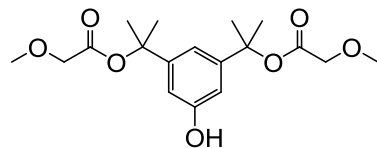
Fischer et al., Chemische Berichte, 28, pp. 3252-58, 1895.

Grignard et al., Compt. Rend., 130, pp. 1322-25, 1900.

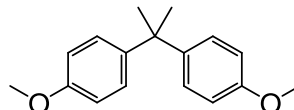
Generation II – Preliminary Lithographic Evaluation



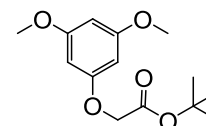
10%



40%

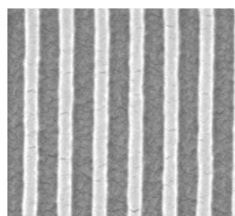


40%

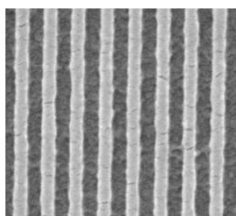


10%

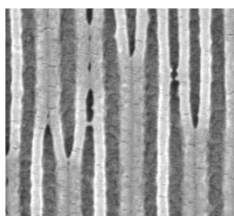
Predicted
T_g = 59 °C



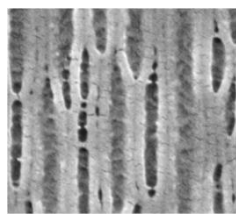
50 nm



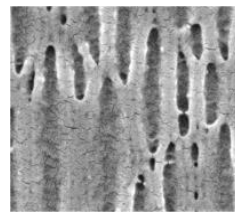
40 nm



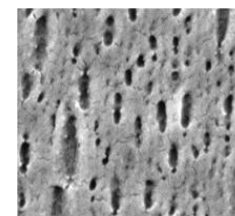
30 nm



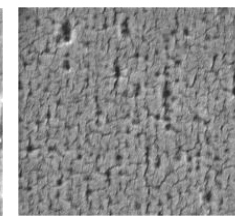
24 nm



20 nm



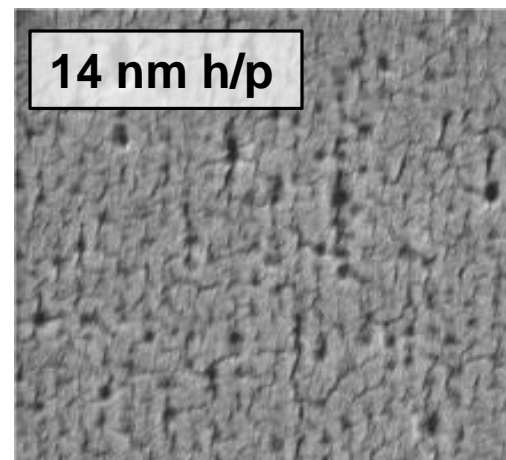
16 nm



14 nm

Dose = 60 mJ/cm² at PEB (none)
Thickness = 40 nm

Although poor image quality was achieved, there does appear to be modulation as low as 14 nm, showing the potential resolution of this system.

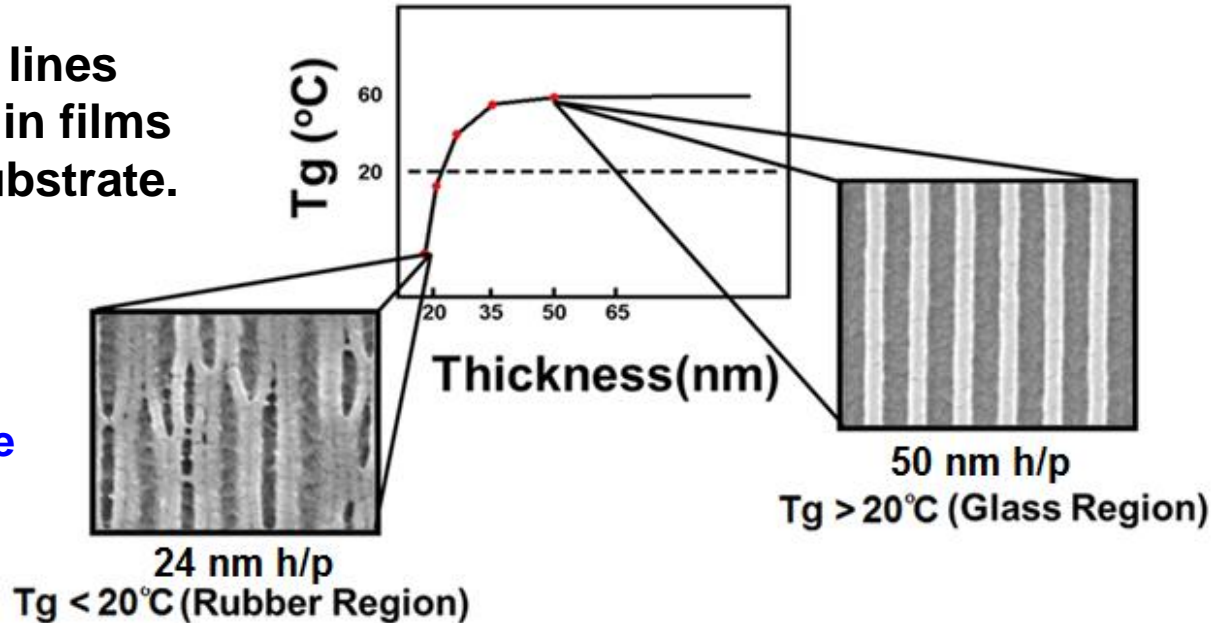
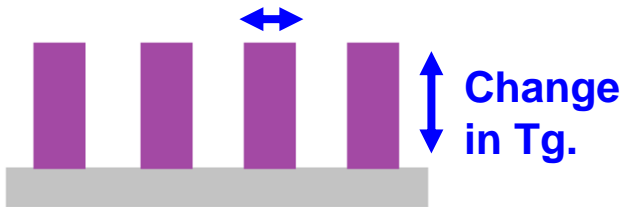


Generation II – Potential Cause of Problems

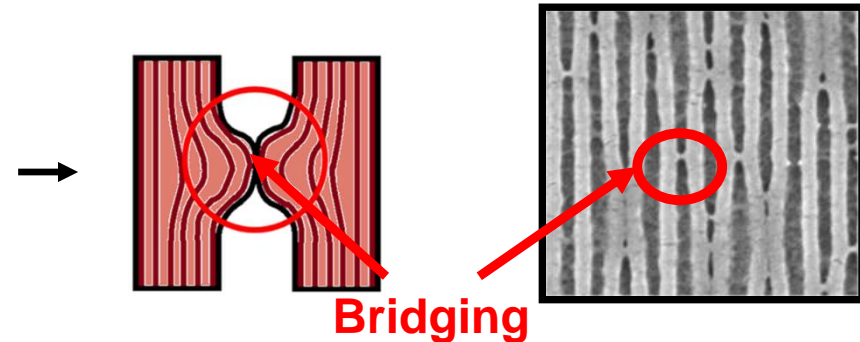
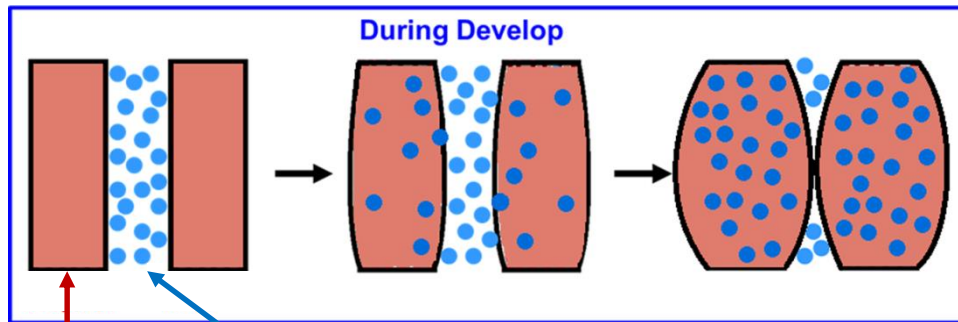
1. Decrease in T_g : T_g can dramatically change in thin films.

After development, the lines can be thought of as thin films perpendicular to the substrate.

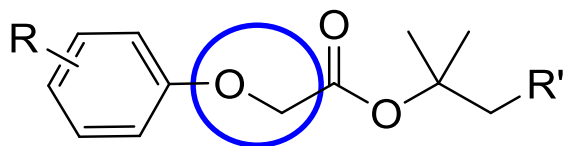
Change in T_g ?



2. Polymer Swelling: Polyethers are commonly hydrogels.

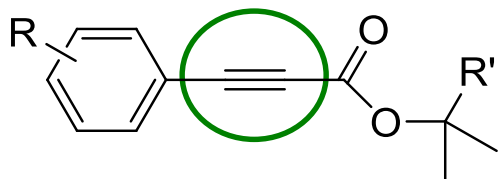


Generation III – Polyalkynes: More Control of Polymer Properties



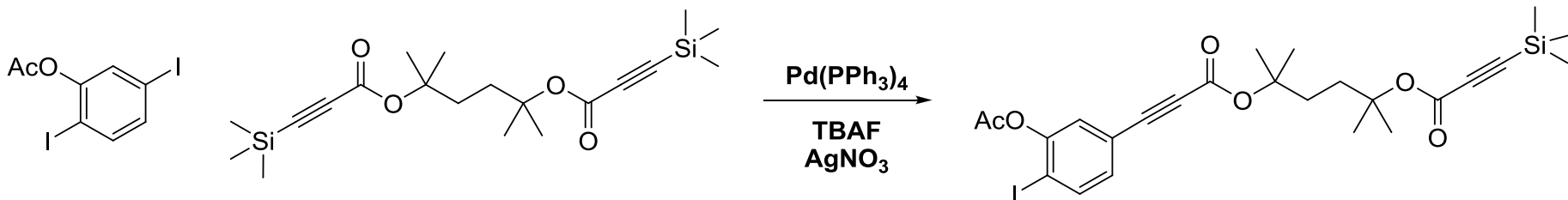
Polyether Linkage

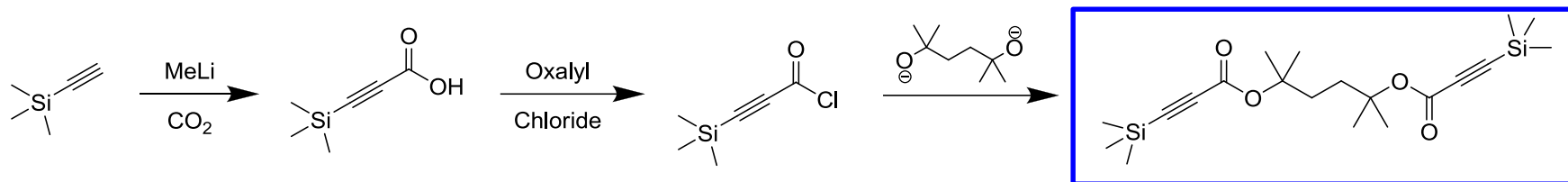
Generation II: Ethers are floppy, hydrogen bonding groups which promote low T_g, hydrophilic polymer properties.



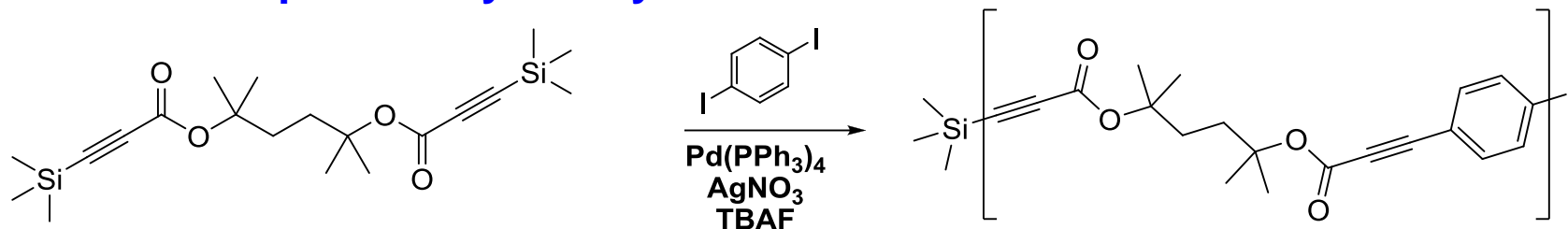
Generation III: Alkynes are rigid, linear and non-polar which should produce high T_g, hydrophobic polymer properties, but there are few polyalkynes of this type in the literature.

Palladium-Catalyzed Hiyama Coupling:



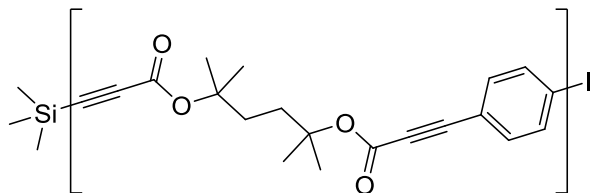


Initial Attempts at Polymer Synthesis:



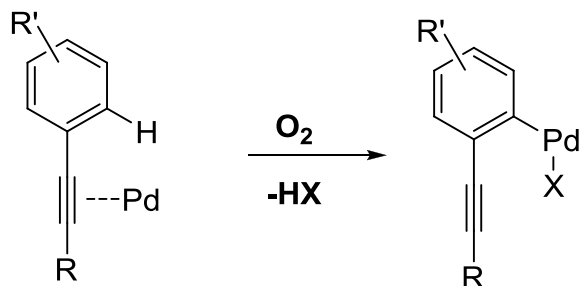
Soluble brown polymer quickly becomes an insoluble black resin...

Polyalkyne Polymerization

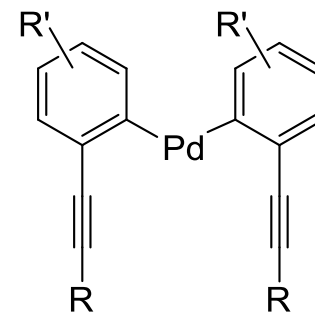


Very few examples of Hiyama polymers of this type in the literature.

Possible Explanation – Ortho-Palladation



Palladation may result in cross-linking of polymer:



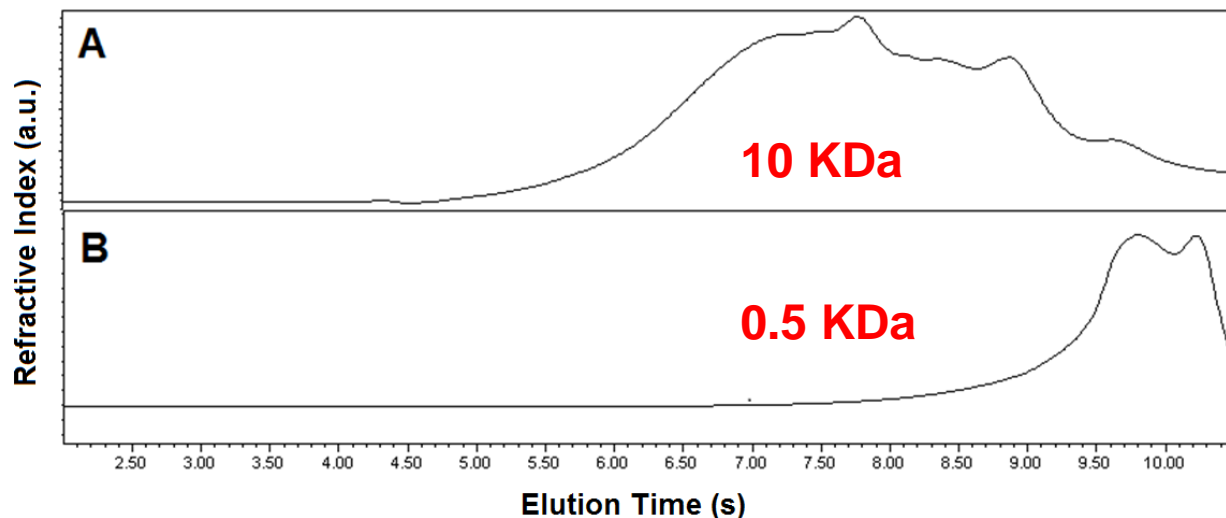
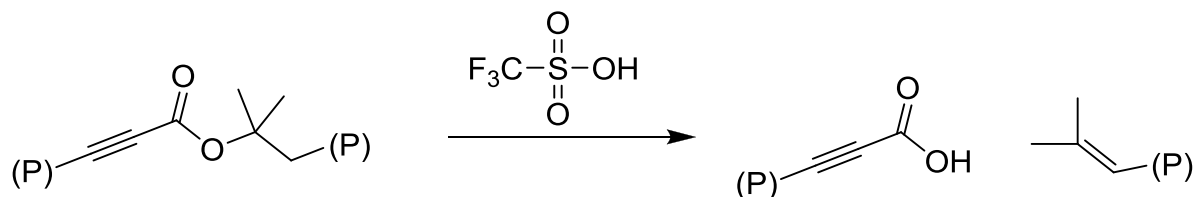
Palladation occurs with oxidized Pd(II)

Polymers can be made more stable by removal of palladium, however cross-linking still occurs. **As of yet no imaging data was obtained for this system.**

Case 1:24-cv-00120-PKS-MJ Document 24-25 Filed 01/11/24 Page 3 of 64

Cleavage of Generation III Polymer

To test chain-scission, strong acid was added to the polymer and then the molecular weight and structure were evaluated by GPC and NMR.



The GPC results show a significant decrease in molecular weight (10 to 0.5 Kda).

Case 1:24-cv-00120-FKS-ML Document 24-35 Filed 01/31/24 Page 24 of 64

Summary – Chain Scission Polymers

Three Generations of Polymer Design Have Been Developed.

Generation I (Polyester Synthesis):

- A set of monomers have been developed and tested.
- Although some promising results, di(acid chloride) monomers were found to be too reactive to yield consistent results.

Generation II (Polyether Condensation):

- A set of monomers have been developed and tested.
- Promising results with high-resolution potentials, but improved physical properties (T_g, hydrophobicity) are needed.

Generation III (Palladium-Catalyzed Polyalkynes):

- A palladium-catalyzed polymerization method has been developed.
- Soluble polymers have been made, but have been found to be unstable and crosslink upon exposure to oxygen.

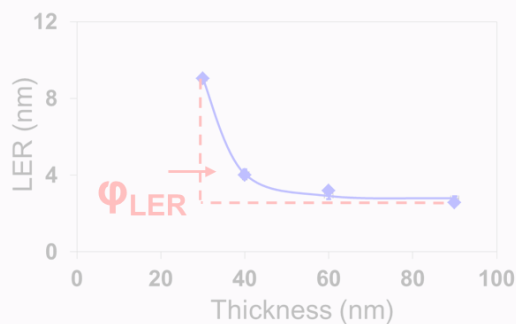
Novel Resist Systems for EUV Lithography: LER, Nanoparticle, Chain-Scission and MORE

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Chemistry:

Synthetic
Chemistry:

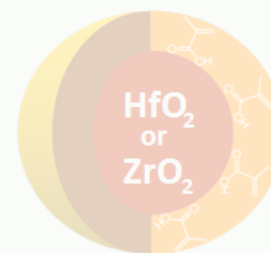
Organic:

LER Degradation

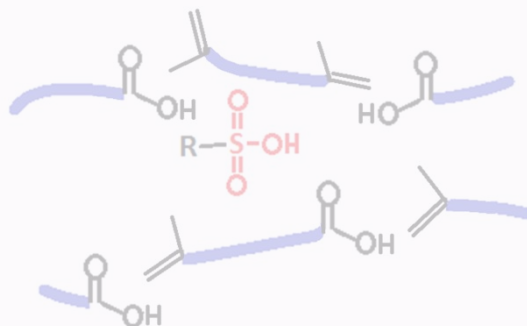


Inorganic:

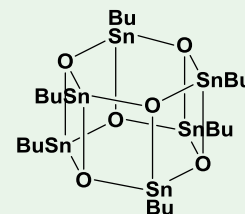
Ligand Design for Hafnium Nanoparticle Resists



Chain Scission Polymers



Molecular Organometallic Resists for EUV (MORE)



III. Introduction: Problems Facing Today's EUV Resists

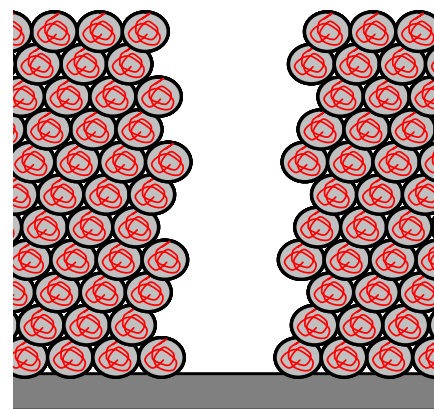
Today's organic chemically amplified resists may be unable to meet the demands of the 16 and 10 nm nodes.

1. Low photon absorption: At thin film thicknesses (~ 20 nm) required, even the darkest, fluorinated polymers only absorb $\sim 20\%$ of photons.

2. Acid diffusion length: If acid diffuses from the exposed to unexposed region, LER can increase drastically.

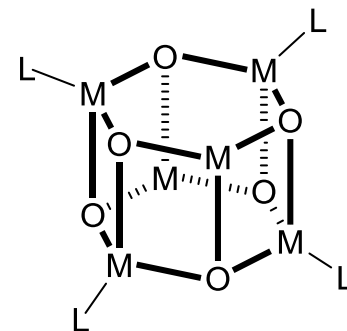
3. Modest etch resistance: As resolution decreases and film thickness decreases, it is becoming progressively harder to etch to the required depth.

4. Resolution approaching polymer radius: LER and resolution are limited by resist polymer radius (~ 1 nm).



MORE Benefits

We have proposed a new platform of resist consisting of high optical density metal oxide organometallic compounds.



Potential Benefits:

1. **High EUV OD:** Using high OD metal oxides (Fe, Co, Sn, Bi, etc.), thin film resists can be made without loss to sensitivity or LER.
2. **High Mass Density:** The mean-free path of secondary-electrons is shorter in high mass-density materials. For resists this would result in a decrease in electron blur.
3. **No Acid Diffusion:** LER increases as acid diffuses into the unexposed region.
4. **Excellent Etch Rates:** Metal oxide films are known to have significantly better etch performance than even the best organic films (HfO_2 ~ 25x better).
5. **High Uncatalyzed Reactivity:** Since metals have a large range of redox potentials, resist chemistry can be engineered for high sensitivity without acid catalysis (no acid diffusion problems).

Electronegativity Atomic Number

2.2 78

Pt

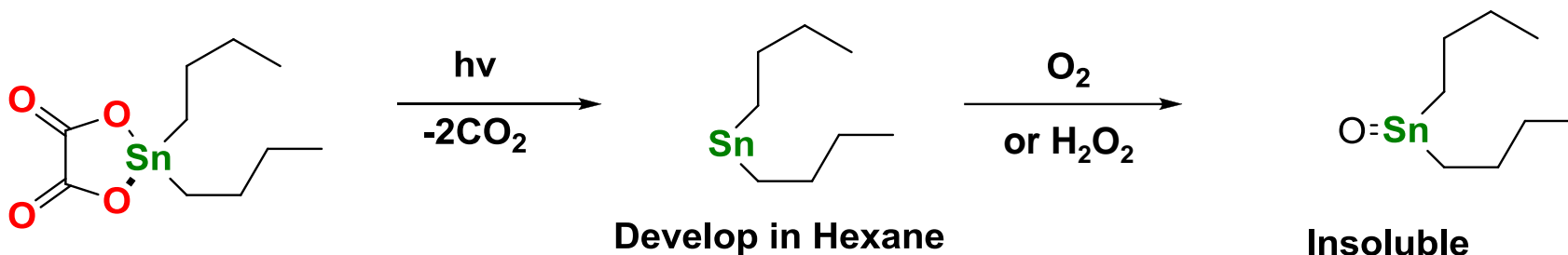
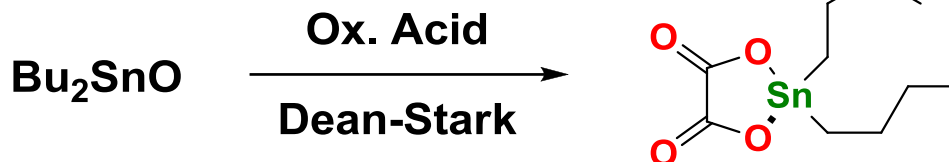
\$

1.1 58 Ce	1.1 59 Pr	1.2 60 Nd	61 Pm \$	1.2 62 Sm	1.2 63 Eu \$	1.1 64 Gd	1.2 65 Tb \$	1.2 66 Dy	1.2 67 Ho	1.2 68 Er	1.2 69 Tm \$	1.1 70 Yb	1.2 71 Lu \$
1.3 90 Th γ	1.5 91 Pa γ	1.7 92 U γ	93 Np γ	94 Pu γ	95 Am γ	96 Cm γ	97 Bk γ	98 Cf γ	99 Es γ	100 Fm γ	101 Md γ	102 No γ	103 Lr γ

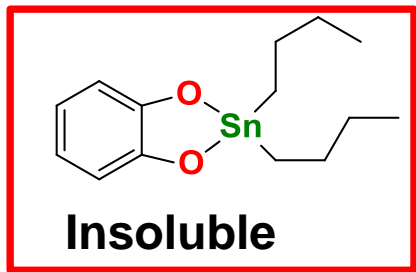
EUV OD at Std. State Density (Relative to Carbon)					
0-2	2-4	4-6	6-8	8-10	10-12

- A. Sn-1 Compounds**
B. Sn-12 Clusters
C. Confidential Results

A. Original Design of Sn-1 Compounds

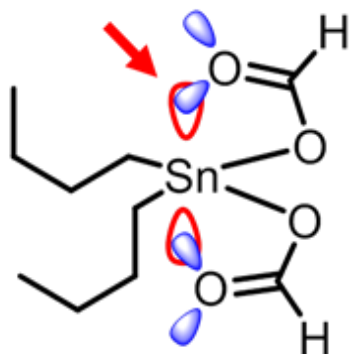


Our original designs of the Sn-1 compounds consisted of forming dibutyltin oxalate which could decompose into the insoluble oxide.



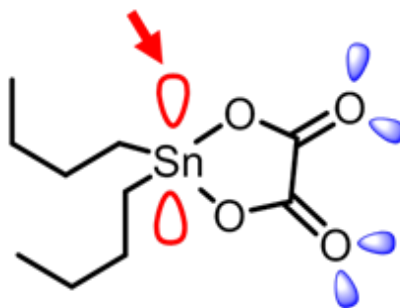
Hypothesis of Sn-1 Compound Solubility

**Sn binding sites
filled by carbonyl
electrons**

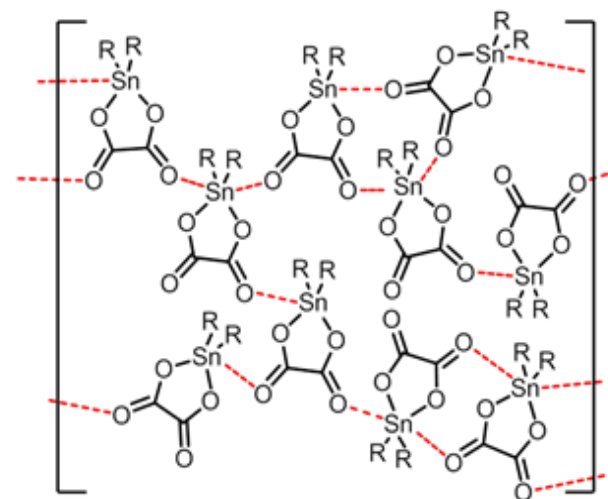


**6-coordinate
Dibutyltin formate**

**Sn binding sites are
left unoccupied.**



**4-coordinate
Dibutyltin oxalate**

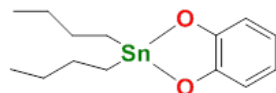
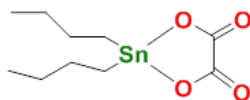


**Possible formation of
insoluble network structure**

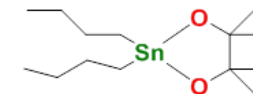
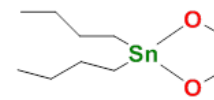
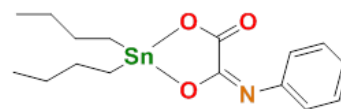
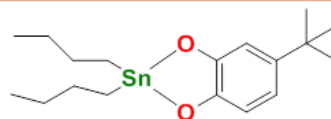
By intramolecular rearrangement, the formate carbonyls can coordinate Sn, making a six-coordinate system.

The oxalate carbonyls however, are constrained from intramolecular rearrangement, resulting in intermolecular cross-linking.

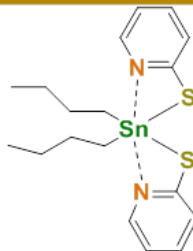
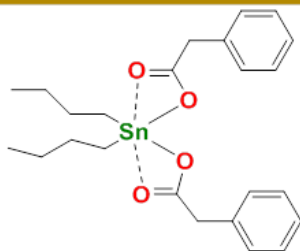
Evaluation of Eleven Sn-1 Compounds



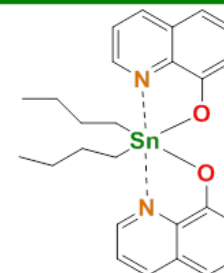
Completely Insoluble



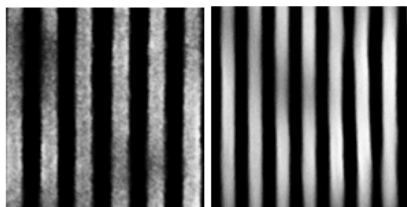
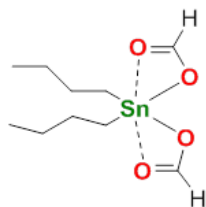
**Mostly Insoluble
Poor Film Quality**



Good Solubility / Crystalline Films

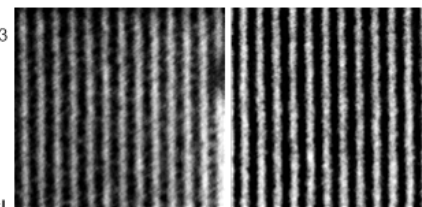
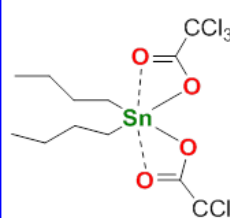


Good Film Quality / No Reactivity



Dose =
50 mJ/cm²

50 35
Resolution h/p (nm)

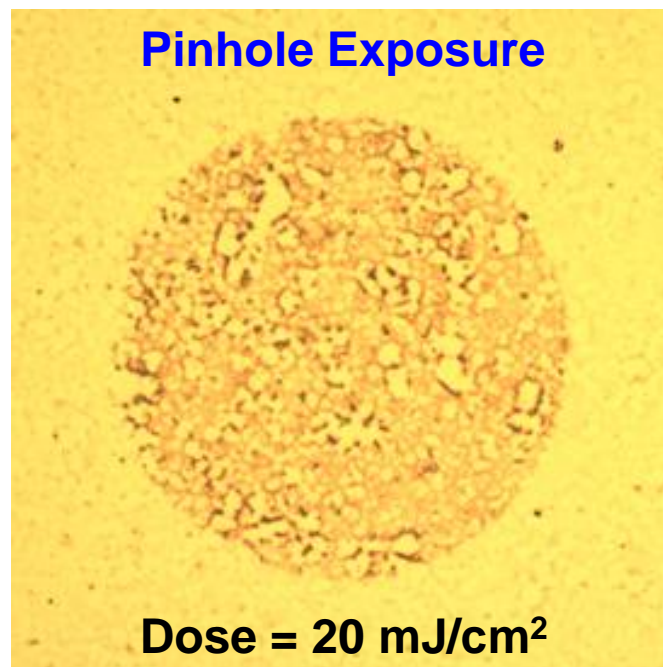
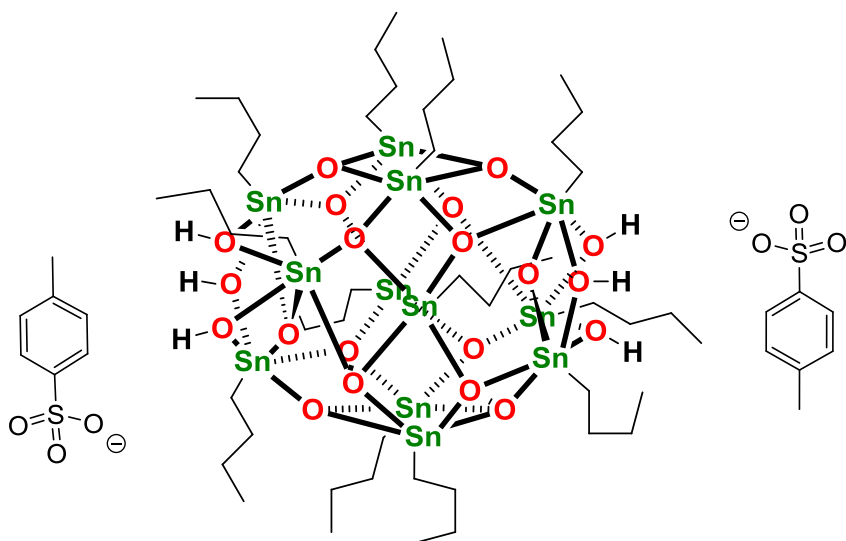


Dose =
190 mJ/cm²

25 18
Resolution h/p (nm)

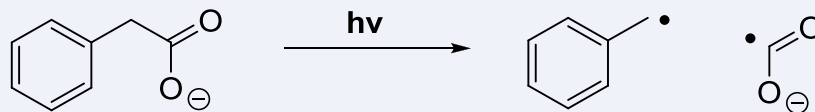
B. Sn-12 Cluster – Preliminary Investigations

Sn-12 Clusters are known in the literature. This was one of several clusters we tested for EUV sensitivity. This one was found to have moderate sensitivity.

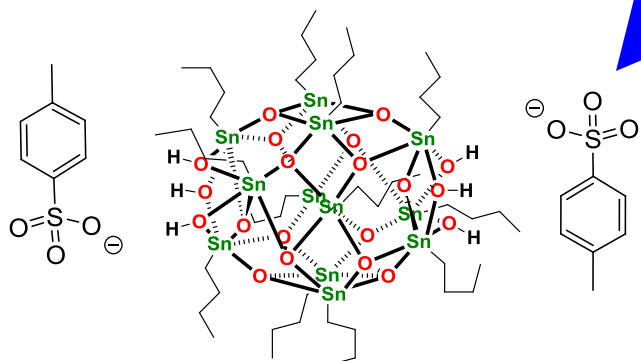


Question: How can we modify this compound to improve its image quality?

Method 1: Counter-Ion Decomposition

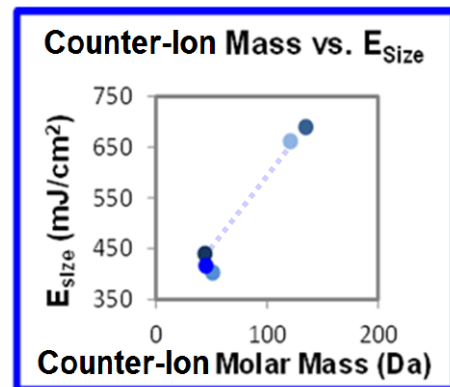
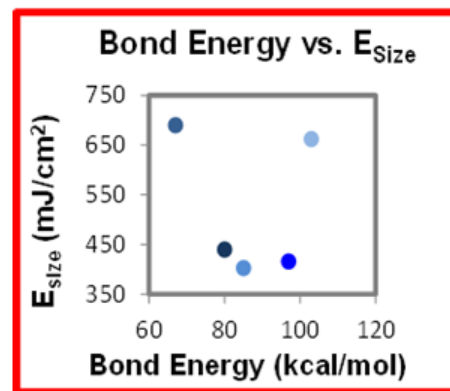
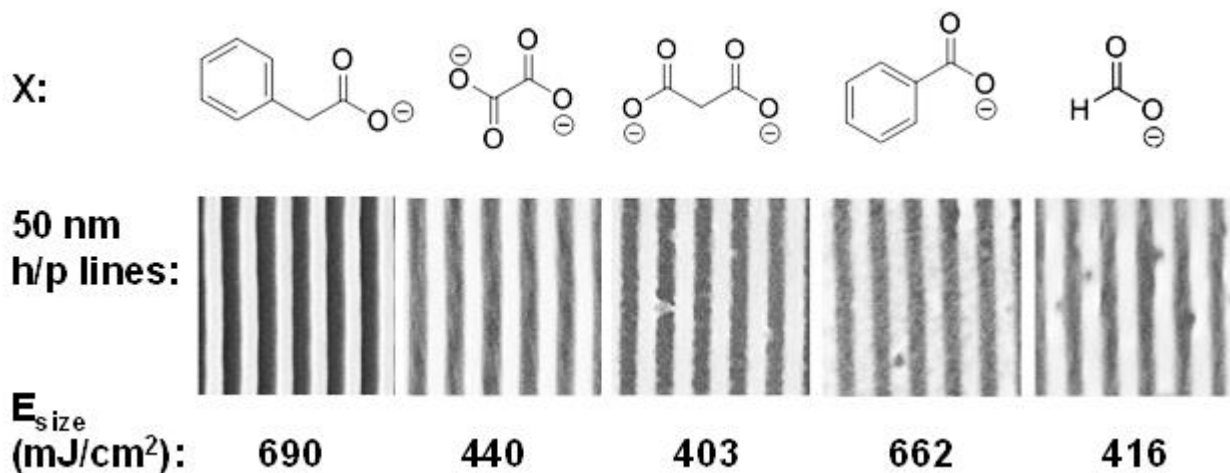
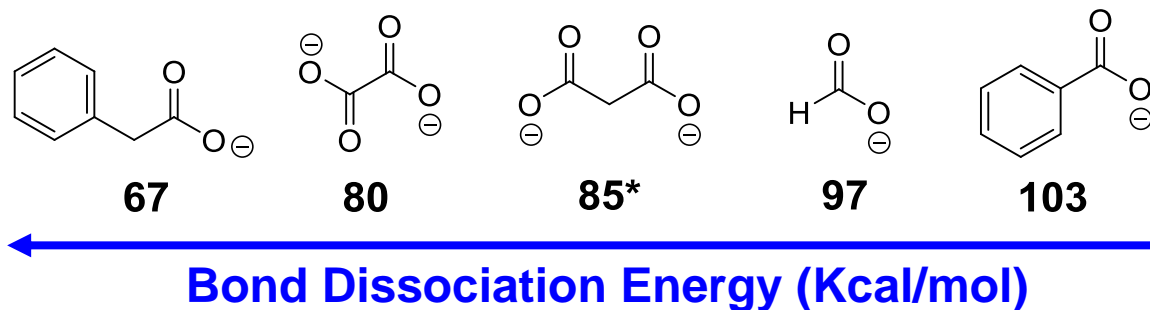
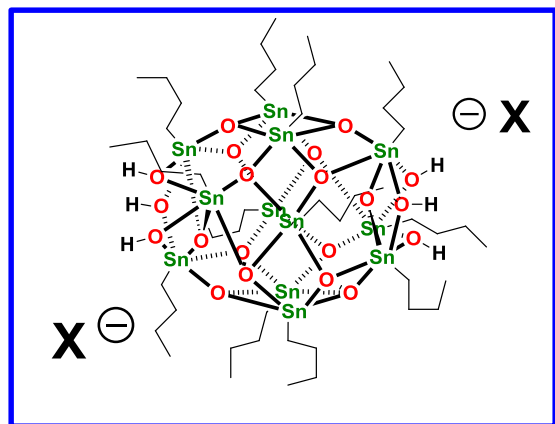


How does the counter-ion structure affect the image quality?

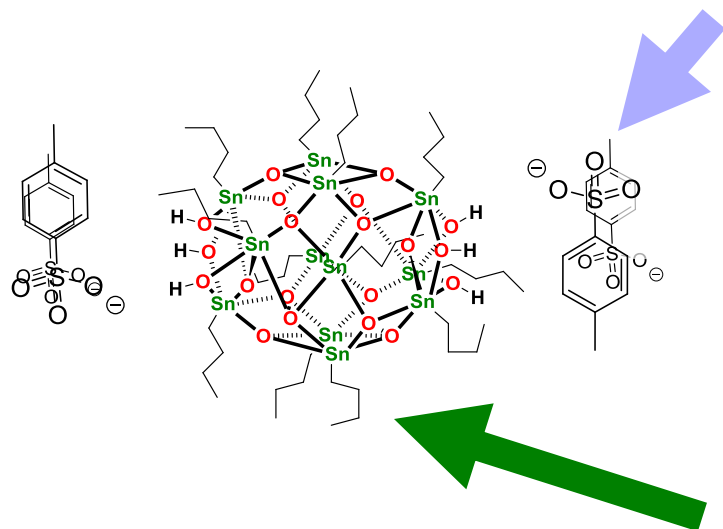


Effect of Counter-Ion Structure on E_{Size}

Case 1:24-cv-00120-BKS-ML Document 24-35 Filed 01/31/24 Page 35 of 64



Question: How can we modify this compound to improve its image quality?

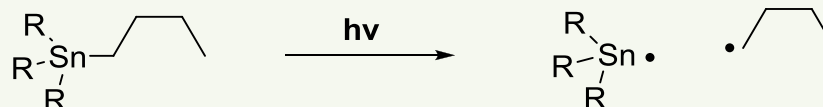


Method 1: Counter-Ion Decomposition



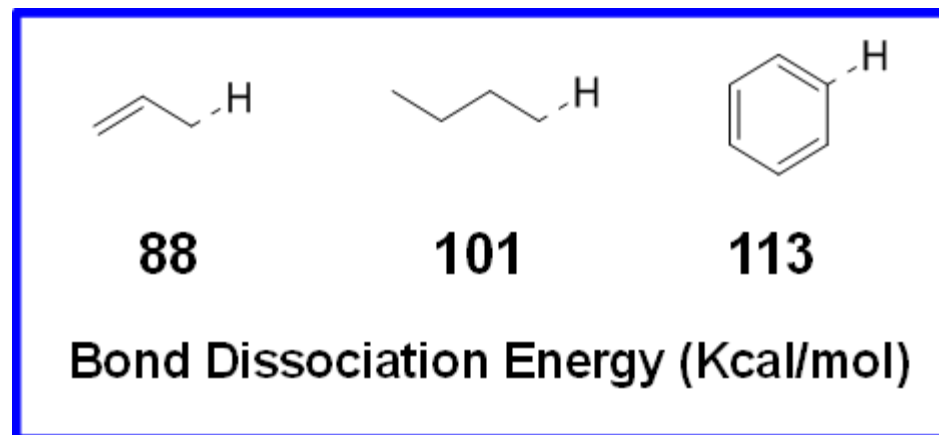
How does the counter-ion structure affect the image quality?

Method 2: Homolysis of Sn-C Bond

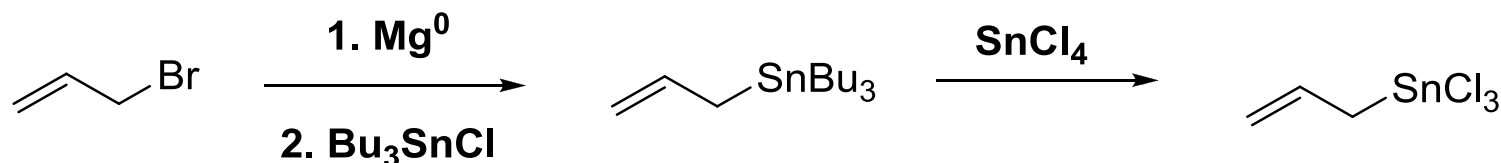


How does changing the organic group affect the image quality?

- Tin is known to form stable radicals.
- Can the cluster sensitivity be sensitized by changing the alkyl group?



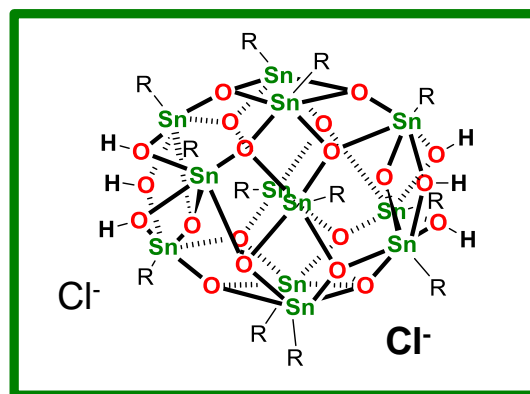
Synthesis of AllylSnCl₃:



Synthesis of Tin Clusters:

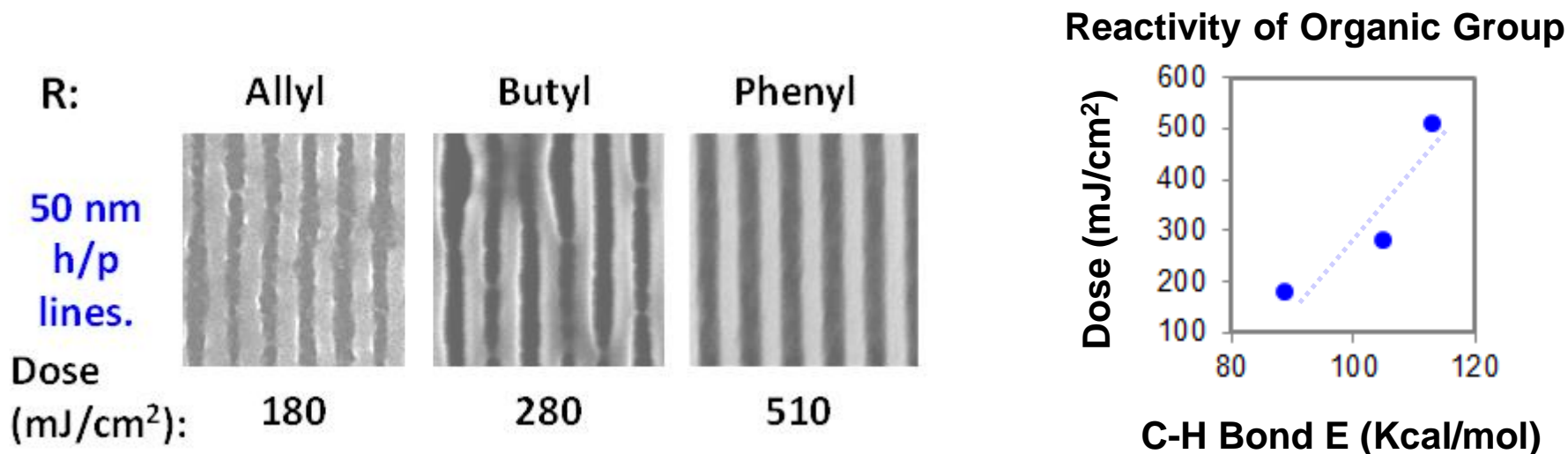


R = Phenyl, Allyl, Butyl



Unable to crystallize.

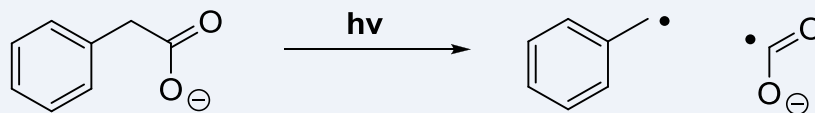
Lithographic Evaluation of Three Sn-12 Clusters



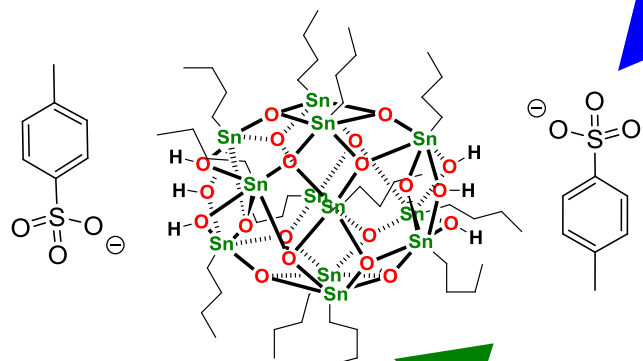
There appears to be a trend in sensitivity with bond energy.

Compound Modification Pathways - Conclusions

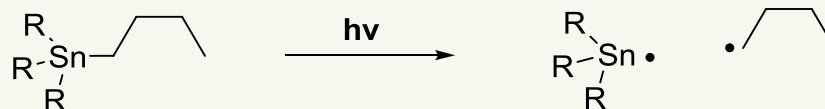
Method 1: Counter-Ion Decomposition



Sensitivity seems to correlate with **molar weight** rather than **bond energy**.



Method 2: Homolysis of Sn-C Bond

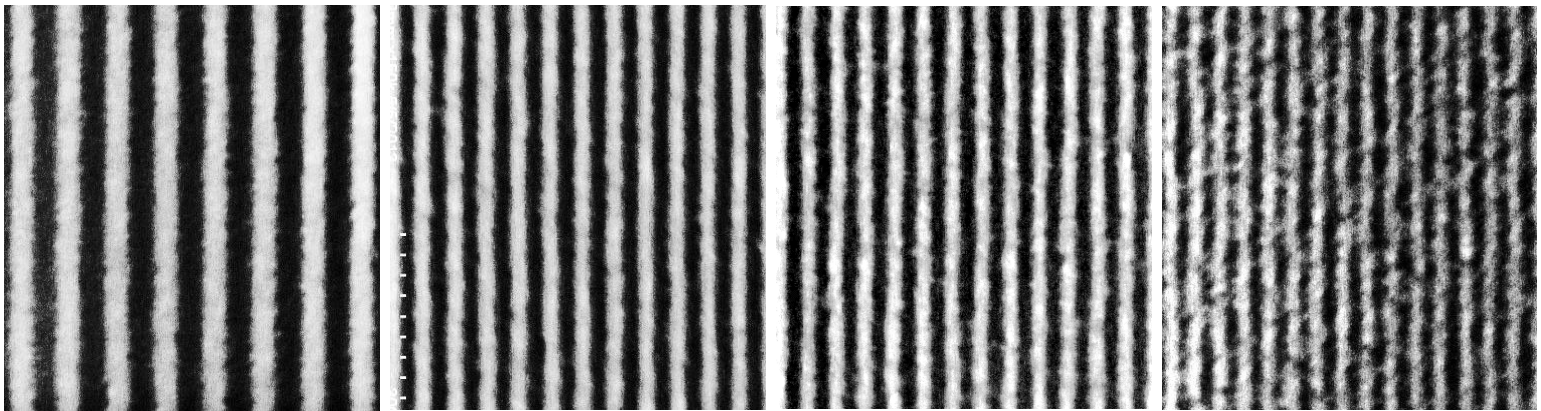


Sensitivity seems to correlate directly with **bond energy**.

C. NP1 – Best Results (Closed Session)

**Structure
Confidential**

Dose of 30 mJ/cm² !



**Resolution
h/p (nm):**

35

25

22

18

LER (nm):

3.0

3.3

4.0

7.1

Thesis Questions

Novel resist design is needed to improve resist performance.

Hypothesis 1: Acid-cleavable chain-scission polymers can be made that function as resists.

- Can acid-cleavable polymers be made and how do they function as resists?
- How do the mechanical and physical properties of the polymer affect the lithographic performance of these chain-scission resists?
- Can high T_g, hydrophilic resist polymers be made using the palladium catalyzed Hiyama coupling reaction?

Hypothesis 2: Molecular-inorganic resists can be made for EUV from high optical-density materials.

- Can inorganic/organometallic compounds act as photoresists?
- How does ligand structure affect performance?
- How do different metals affect performance? (will be discussed in a closed session.)

Acid-Cleavable Chain-Scission Polymers can be Made that Function as Resists.

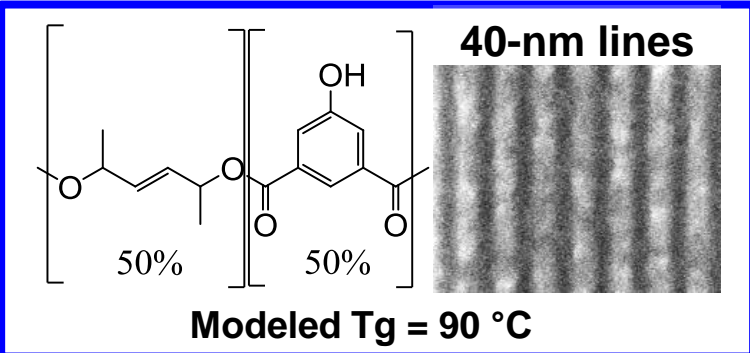
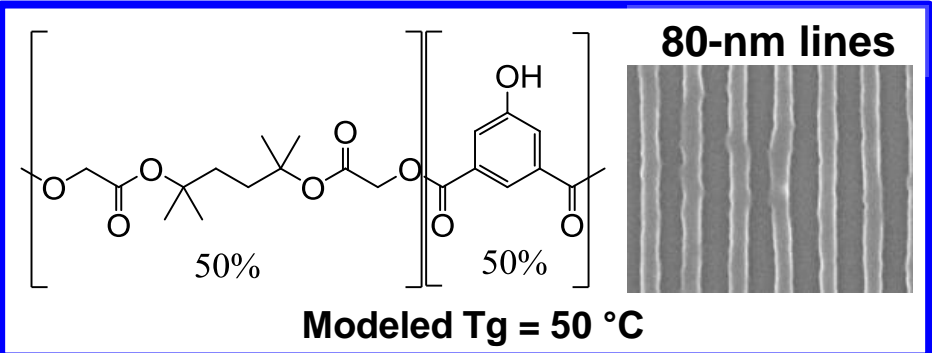
- Can acid-cleavable polymers be made and how do they function as resists?

Generation I
Polyesters showed some promising results but had poor reproducibility.

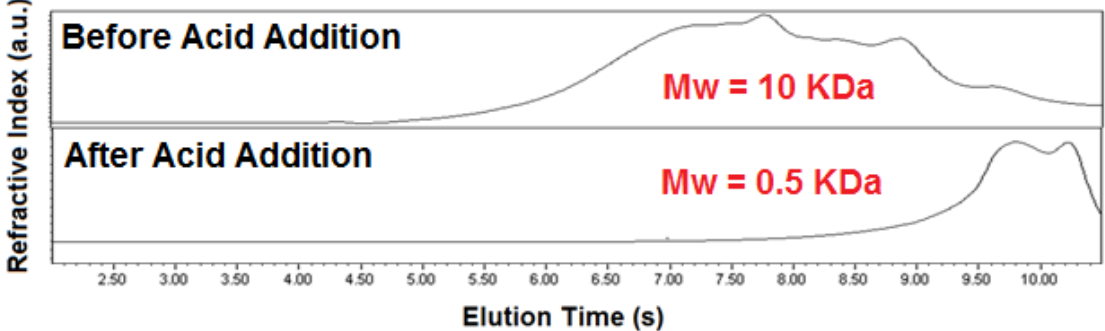
Generation II
Polyethers showed high resolution imaging, but low Tg and high hydrophobicity were problematic

Generation III
Polyalkynes were made and found to be acid-cleavable, but residual palladium caused crosslinking

- How do the mechanical and physical properties of the polymer affect the lithographic performance of these chain-scission resists?



- Can high Tg, hydrophilic resist polymers be made using the palladium catalyzed Hiyama coupling reaction?



Acid-Cleavable Chain-Scission Polymers can be Made that Function as Resists.

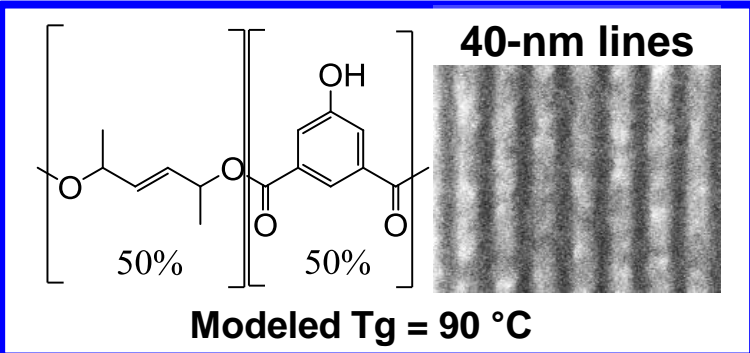
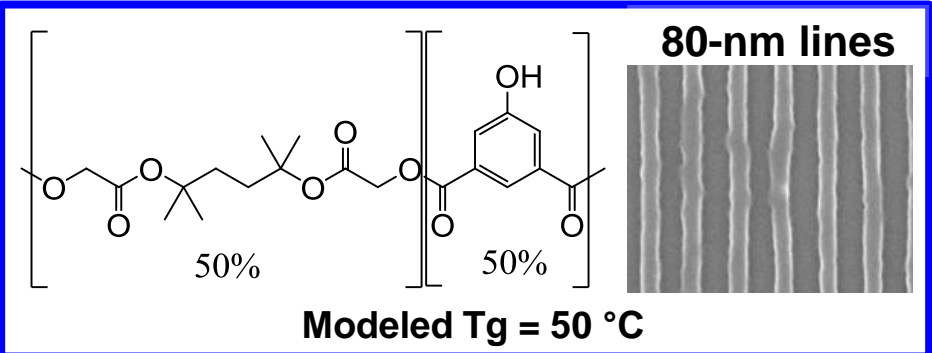
- Can acid-cleavable polymers be made and how do they function as resists? **Yes**

Generation I
Polyesters showed some promising results but had poor reproducibility.

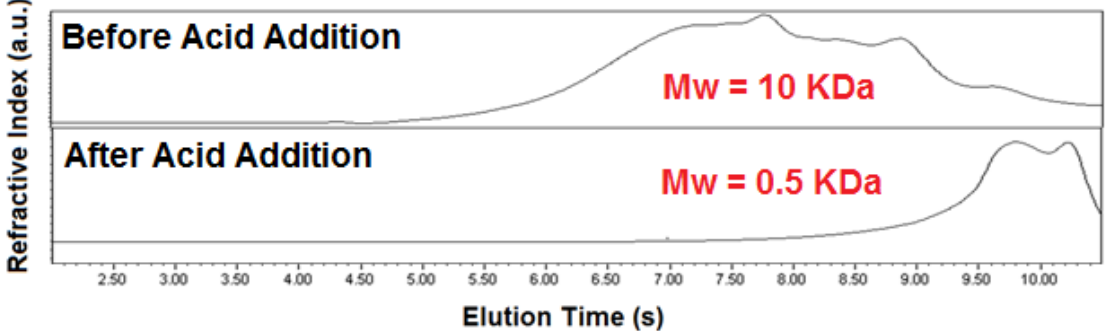
Generation II
Polyethers showed high resolution imaging, but low Tg and high hydrophobicity were problematic

Generation III
Polyalkynes were made and found to be acid-cleavable, but residual palladium caused crosslinking

- How do the mechanical and physical properties of the polymer affect the lithographic performance of these chain-scission resists?



- Can high Tg, hydrophilic resist polymers be made using the palladium catalyzed Hiyama coupling reaction?



Acid-Cleavable Chain-Scission Polymers can be Made that Function as Resists.

- Can acid-cleavable polymers be made and how do they function as resists? **Yes**

Generation I
Polyesters showed some promising results but had poor reproducibility.

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Polyethers showed high resolution imaging, but low Tg and high hydrophobicity were problematic

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Polyalkynes were made and found to be acid-cleavable, but residual palladium caused crosslinking

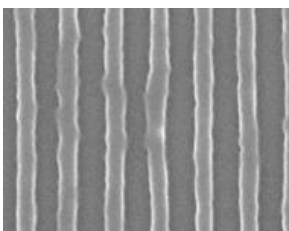
- How do the mechanical and physical properties of the polymer affect the lithographic performance of these chain-scission resists? **Increasing Tg improves performance**

O=C(OCCOC(C)(C)CC(C)(C)OC(=O)COC(=O)c1ccc(O)cc1)C(=O)

50% 50%

Modeled Tg = 50 °C

80-nm lines

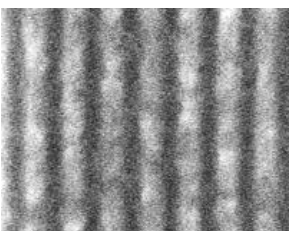


O=C(OCCOC(C)C/C=C/C(C)COC(=O)COC(=O)c1ccc(O)cc1)C(=O)

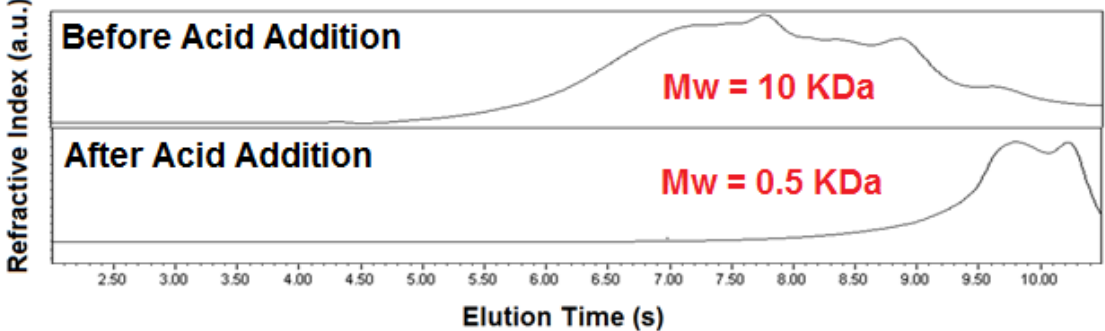
50% 50%

Modeled Tg = 90 °C

40-nm lines



- Can high Tg, hydrophilic resist polymers be made using the palladium catalyzed Hiyama coupling reaction?



Acid-Cleavable Chain-Scission Polymers can be Made that Function as Resists.

- Can acid-cleavable polymers be made and how do they function as resists? **Yes**

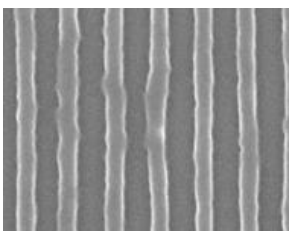
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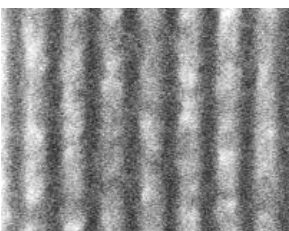
- How do the mechanical and physical properties of the polymer affect the lithographic performance of these chain-scission resists? **Increasing Tg improves performance**

O=C(c1ccc(O)cc1)OC(=O)OC(C)(C)CC(C)(C)OC(=O)O
50%
50%

80-nm lines


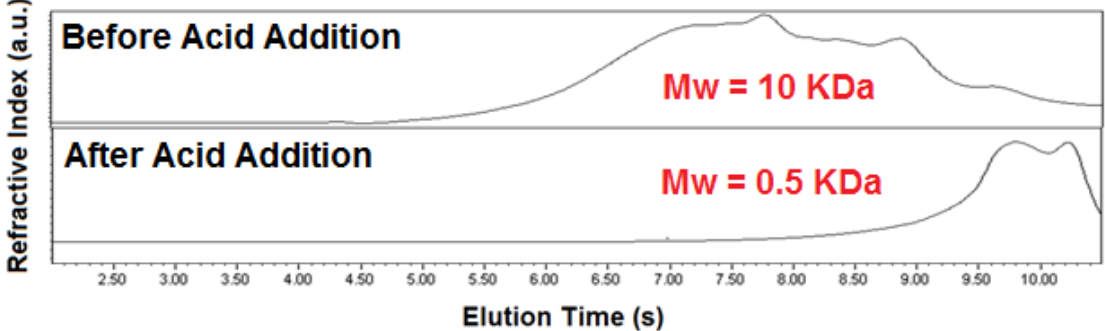
Modeled Tg = 50 °C

O=C(c1ccc(O)cc1)OC(=O)OC(C)C=C(C)OC(=O)O
50%
50%

40-nm lines


Modeled Tg = 90 °C

- Can high Tg, hydrophilic resist polymers be made using the palladium catalyzed Hiyama coupling reaction? **Probably, but these polymers are unstable**

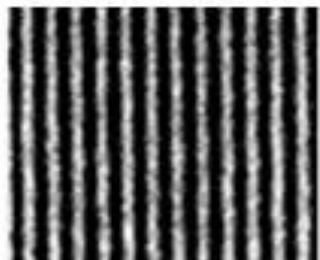


Molecular-Inorganic Resists can be Made for EUV from High Optical-Density Materials.

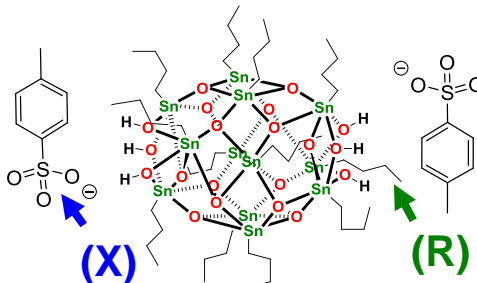
- Can inorganic/organometallic compounds act as photoresists?

Sn-1 Compounds

18 nm // 190 mJ/cm²

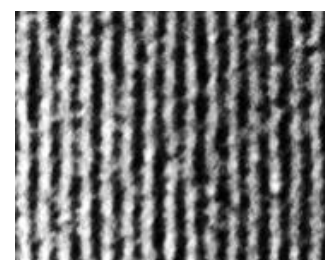


Sn-12 Clusters



Confidential Materials

18 nm // 30 mJ/cm²



- How does ligand structure affect performance?

Sn-1 Compounds

Ligand structure affects:

- Solubility
- Crystallinity
- Resolution
- Sensitivity

Resolution (nm):

18

35

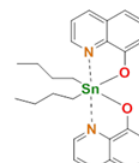
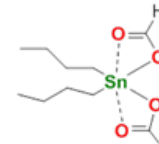
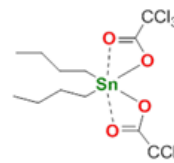
-

Sensitivity (mJ/cm²):

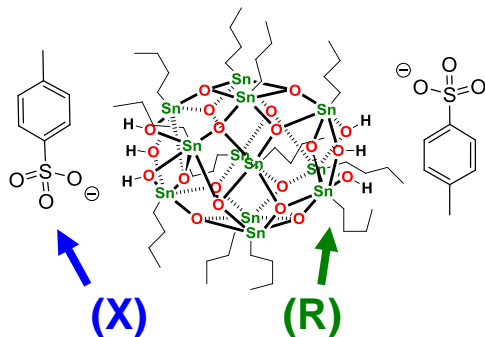
190

50

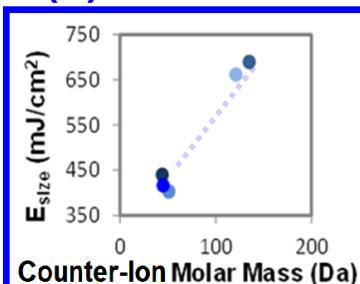
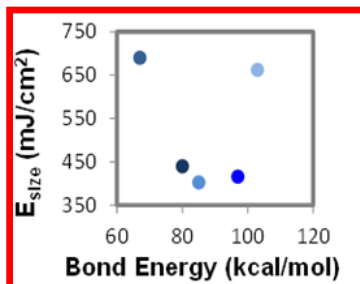
-



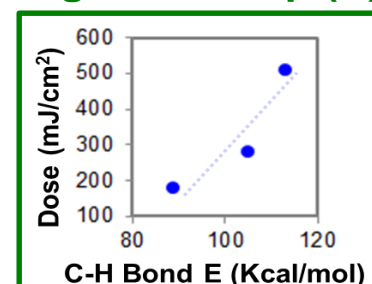
Sn-12 Clusters



Counter Ion (X)

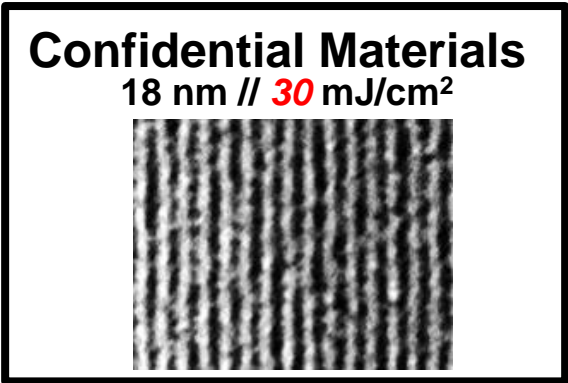
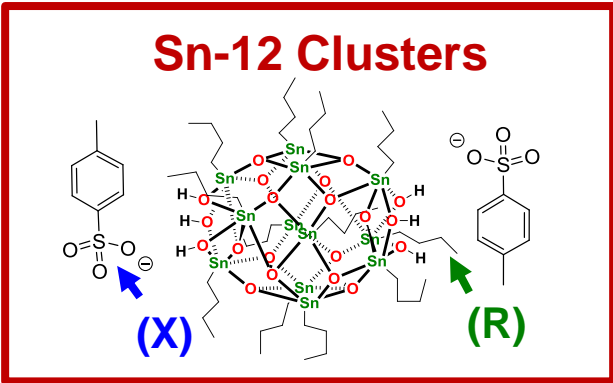
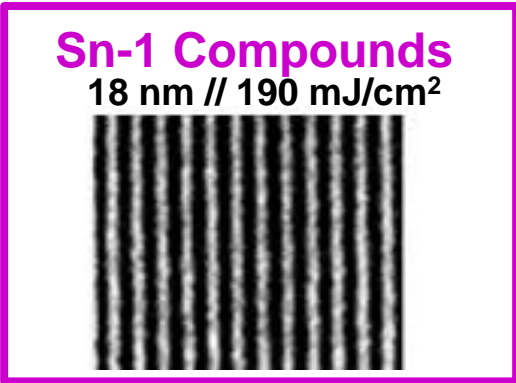


Organic Group (R)



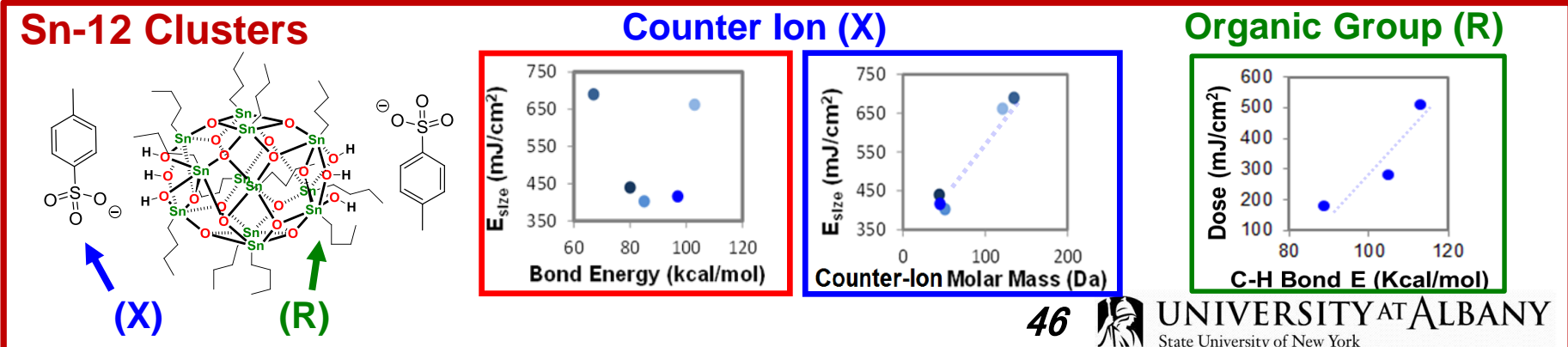
Molecular-Inorganic Resists can be Made for EUV from High Optical-Density Materials.

- Can inorganic/organometallic compounds act as photoresists? **Yes**



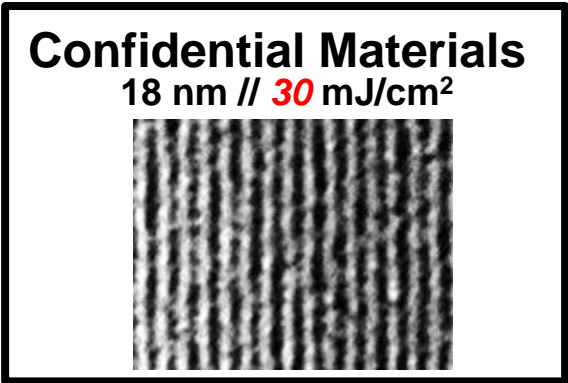
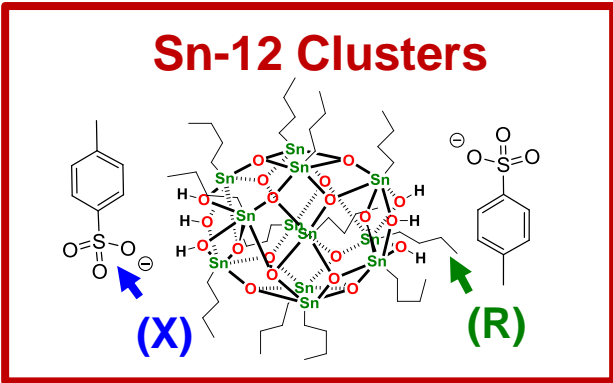
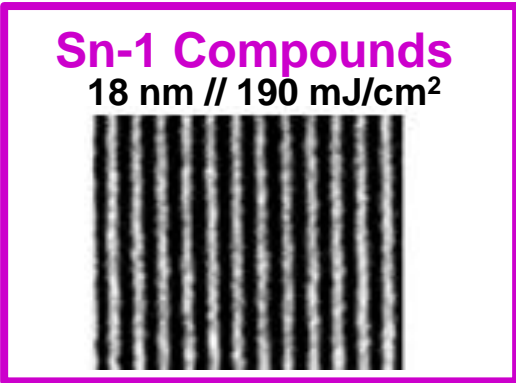
- How does ligand structure affect performance?

Sn-1 Compounds			
Ligand structure affects:			
<ul style="list-style-type: none">SolubilityCrystallinityResolutionSensitivity	Resolution (nm):	18	35
	Sensitivity (mJ/cm ²):	190	50



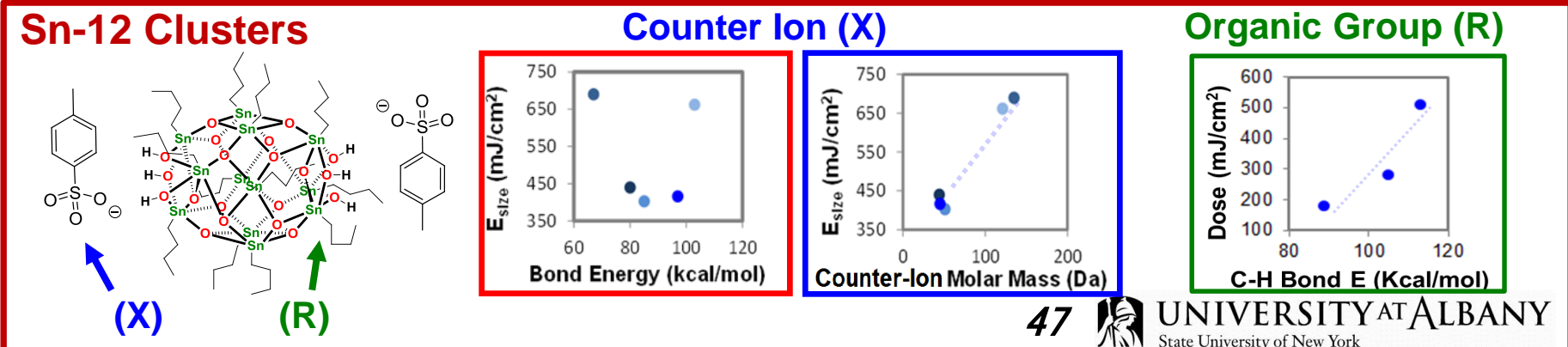
Molecular-Inorganic Resists can be Made for EUV from High Optical-Density Materials.

- Can inorganic/organometallic compounds act as photoresists? **Yes**



- How does ligand structure affect performance? **Ligand Structure affects solubility, crystallinity, resolution and sensitivity**

Sn-1 Compounds			
Ligand structure affects:			
• Solubility			
• Crystallinity			
• Resolution			
• Sensitivity			
	Resolution (nm):	18	35
	Sensitivity (mJ/cm ²):	190	50



Acknowledgements

Advisor

Robert Brainard

Committee Members

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Seth Kruger

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Lauren Sfakis

Miles Marnell

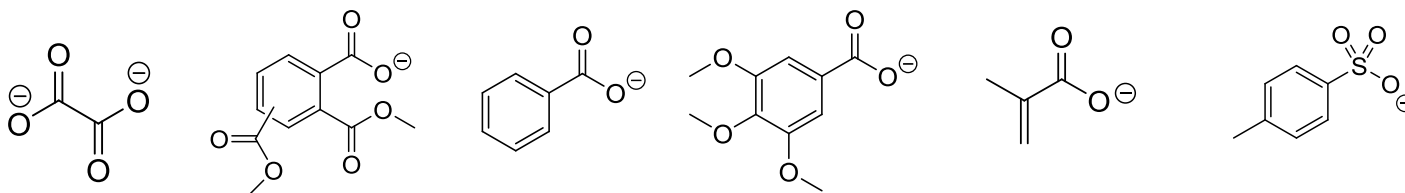
Kara Heard

Amber Aslam

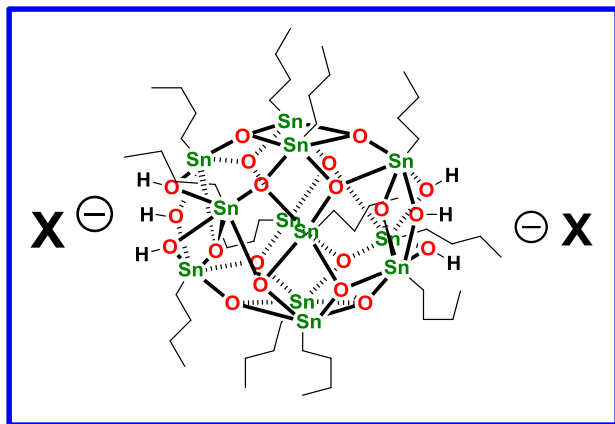
Hashim Al-Mashat

Appendix

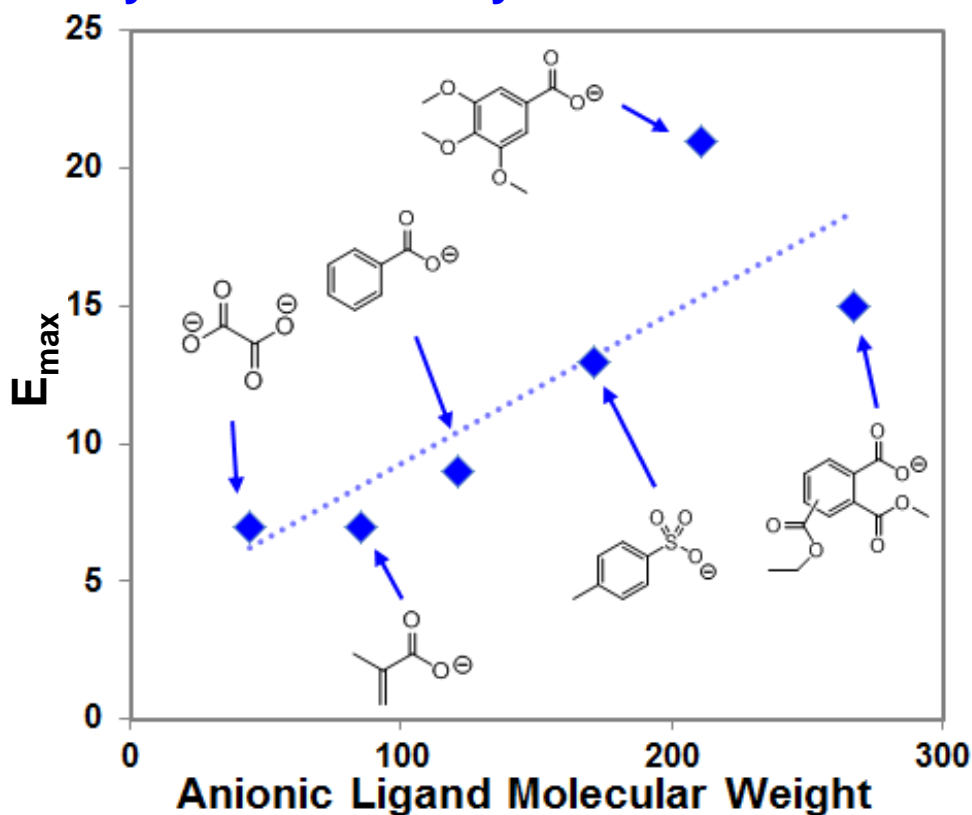
BMET Results: Contrast Curves



Expected Decarboxylation Reactivity

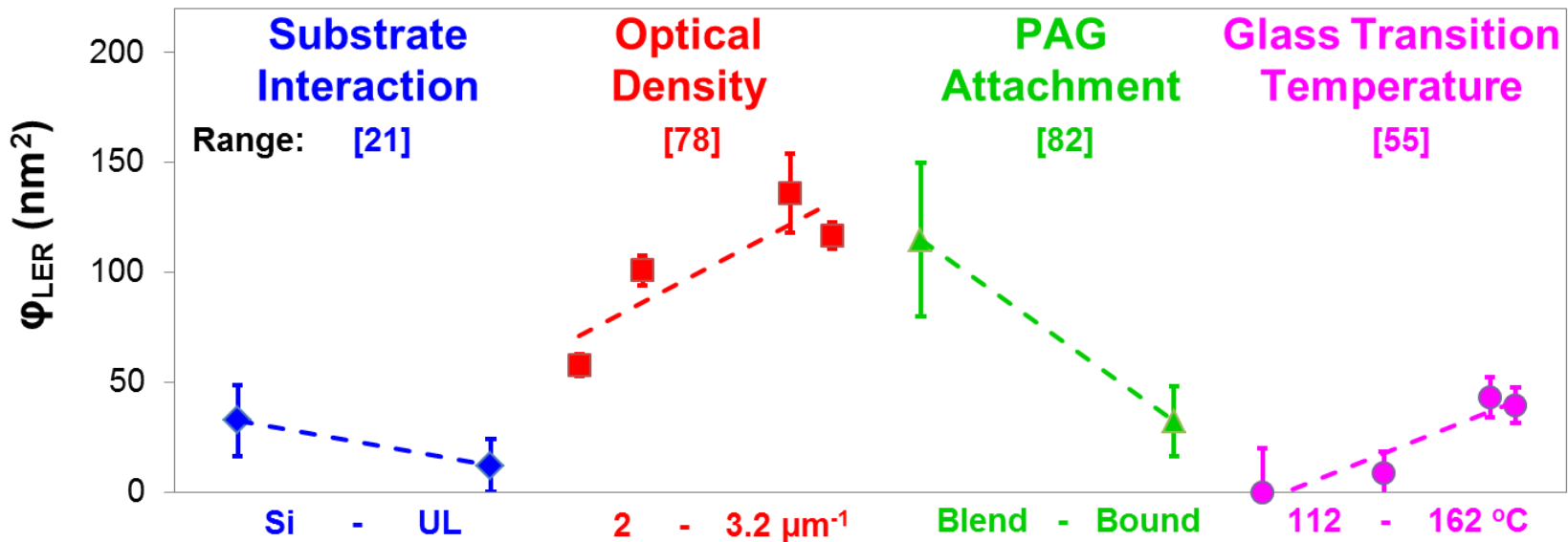
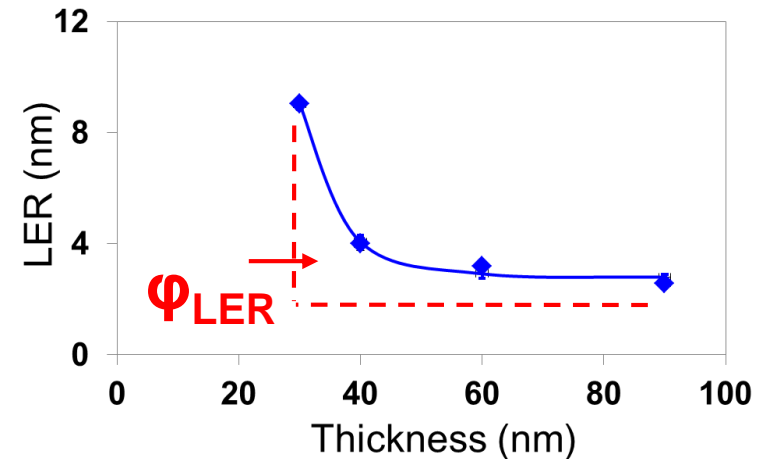
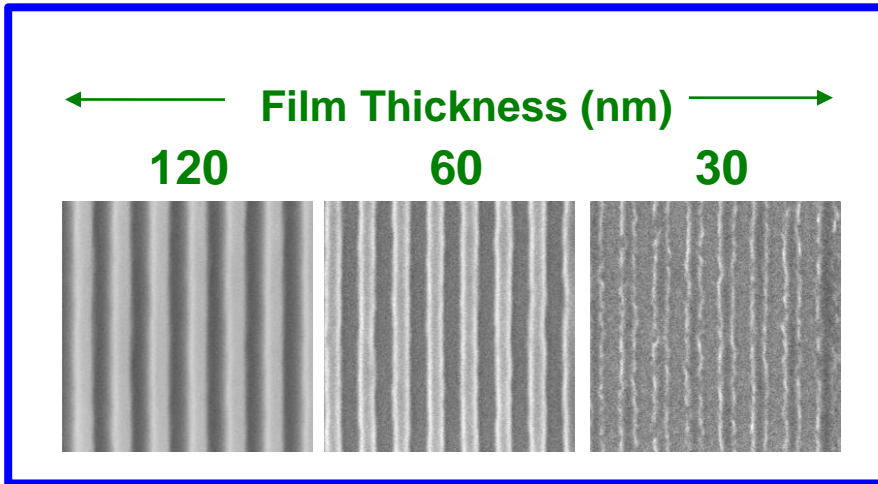


The resist sensitivity seems to be affected more by ligand bulk and less by decarboxylative reactivity.



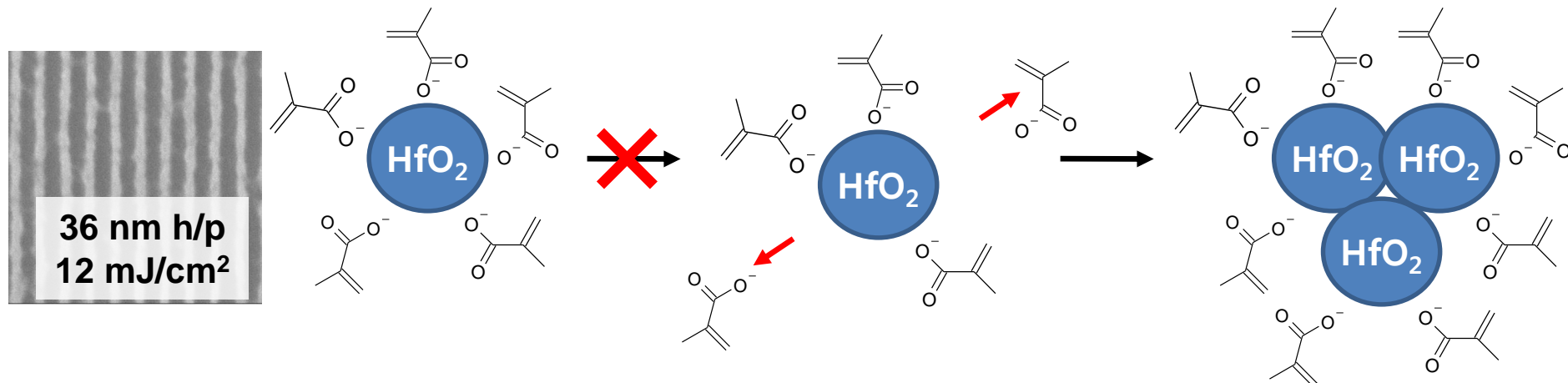
LER Degradation as a Function of Film Thickness

Objective: To study the root-cause of the phenomenon of LER degradation as a function of film thickness.

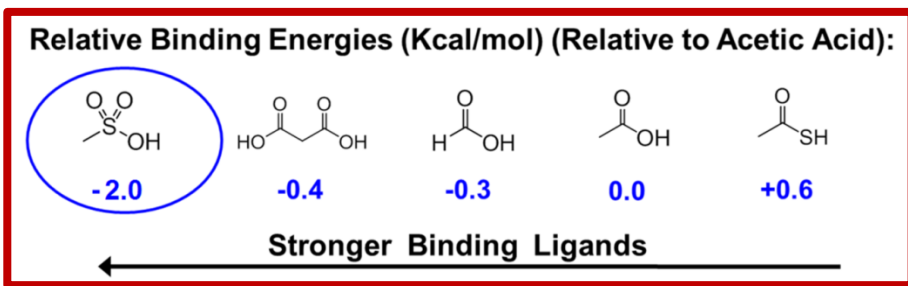


Ligand Design for Hafnium Nanoparticle Resists

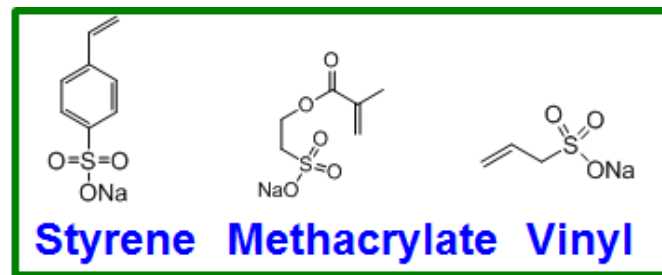
Objective: To help Cornell further understand the ligand / nanoparticle interaction of their Hafnium resist systems and to develop new ligands for this system.



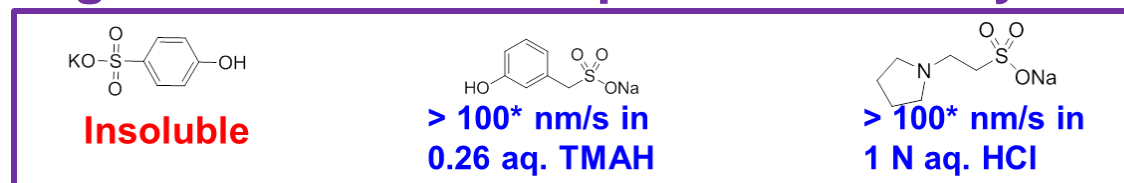
NMR Ligand Binding Study:



Free-Radical Monomer Ligands:



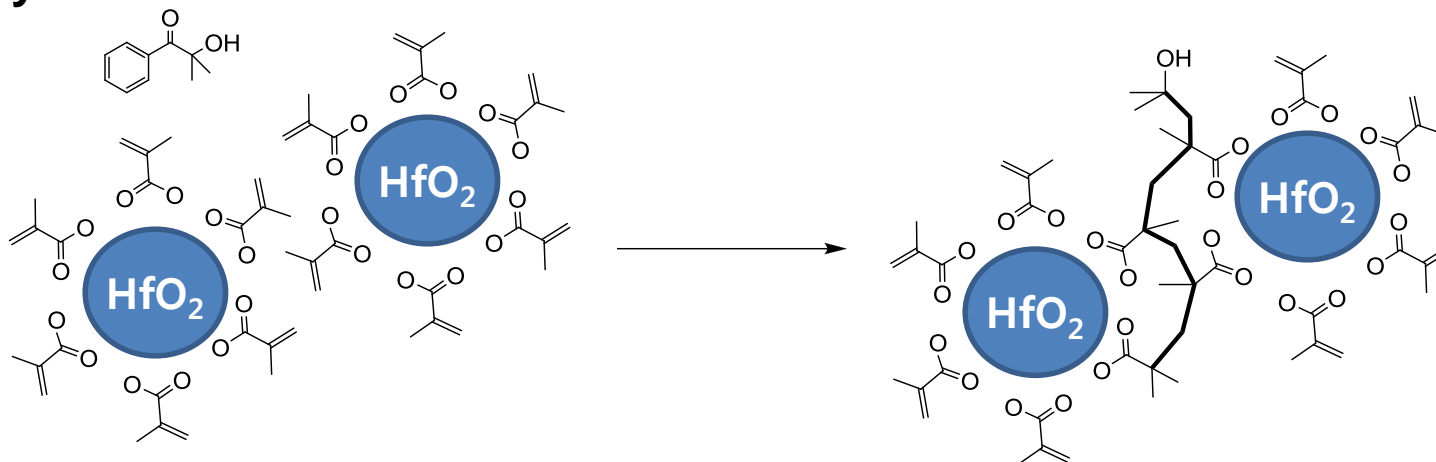
Ligands to Promote Aqueous Solubility:



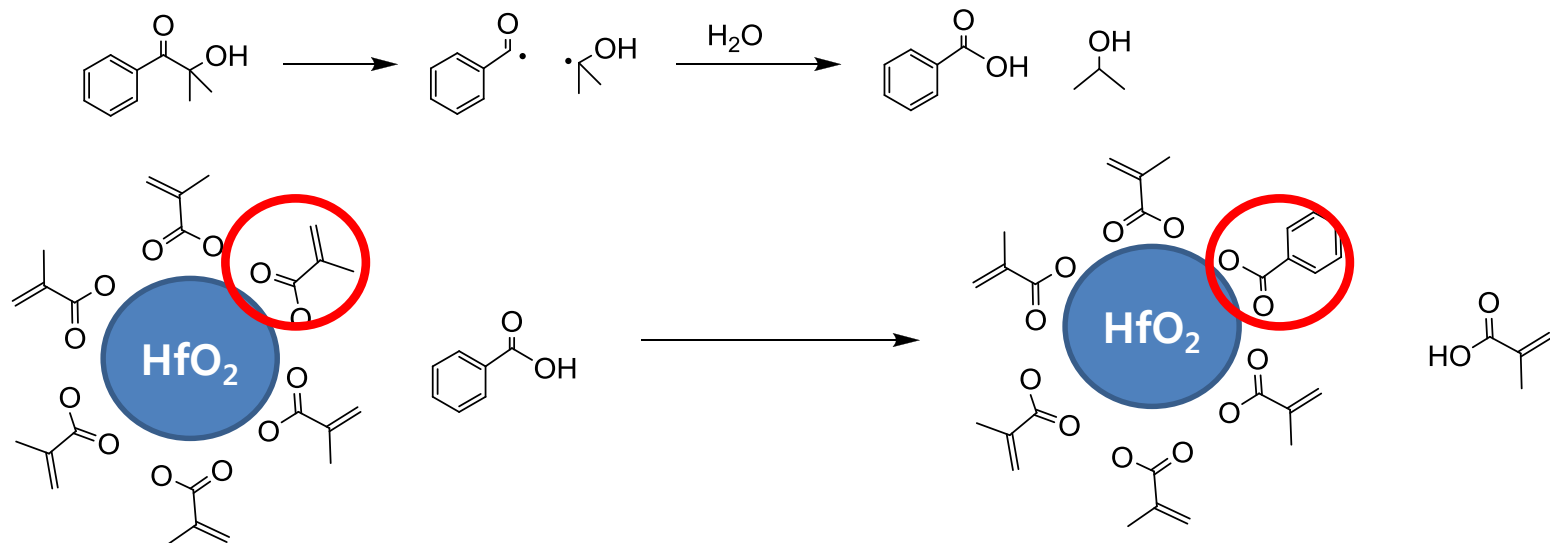
Case 1:24-cv-00120-BKS-ML Document 24-35 Filed 01/31/24 Page 52 of 64

Nanoparticle Mechanism Revision

Originally Intended Mechanism:



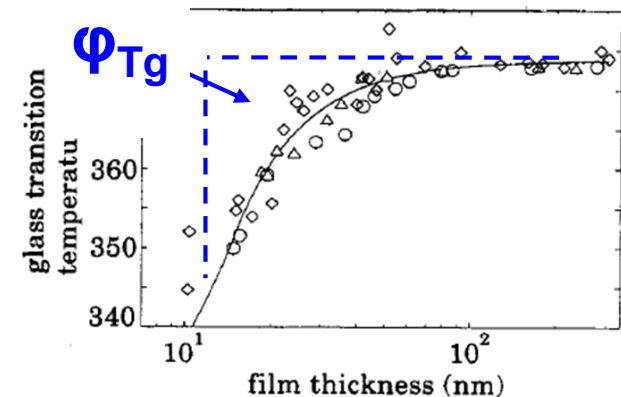
Revised Mechanism:



Keddie Model for T_g as a function of film thickness:

$$T_g(d) = T_{g\infty} \left[1 - \left(\frac{A}{d} \right)^\delta \right]$$

Keddie et al., Europhysics Letters, 27(1), pp. 59-64, 1994.



CNSE Model for LER as a function of film thickness:

$$LER(d) = LER_{\infty} \left[1 + \left(\frac{A'}{d} \right)^{\delta'} \right]$$

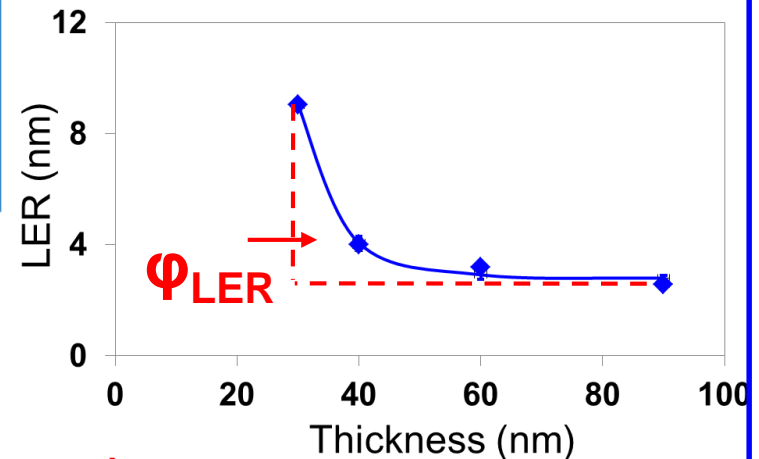
LER_{∞} = Bulk LER

A' = Thickness Dependence

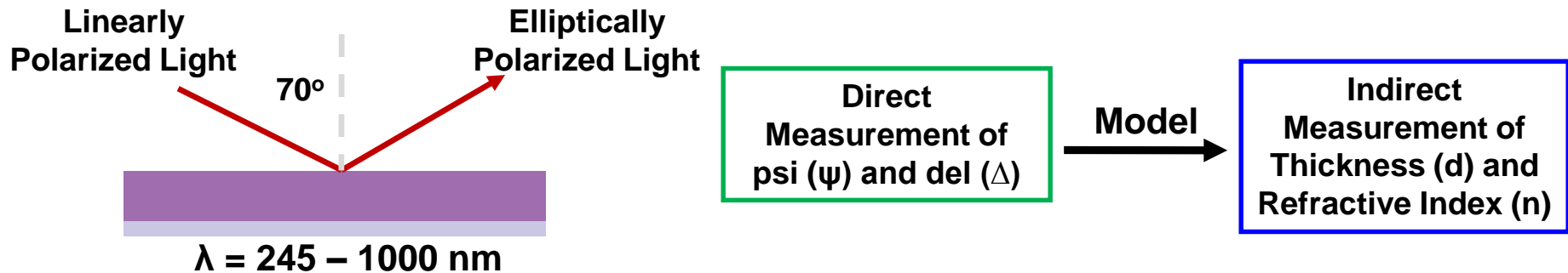
δ' = Exponential

ϕ = Area under LER curve

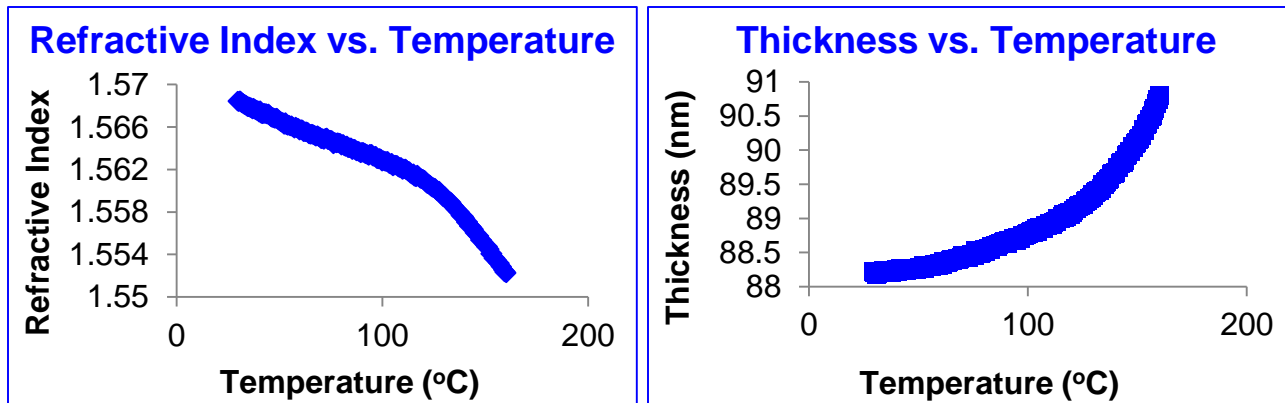
(Smaller $\phi \rightarrow$ Better LER thickness dependence)



Basic Ellipsometry:



Glass Transition (T_g): Temperature at which a polymer can overcome cohesive energy.

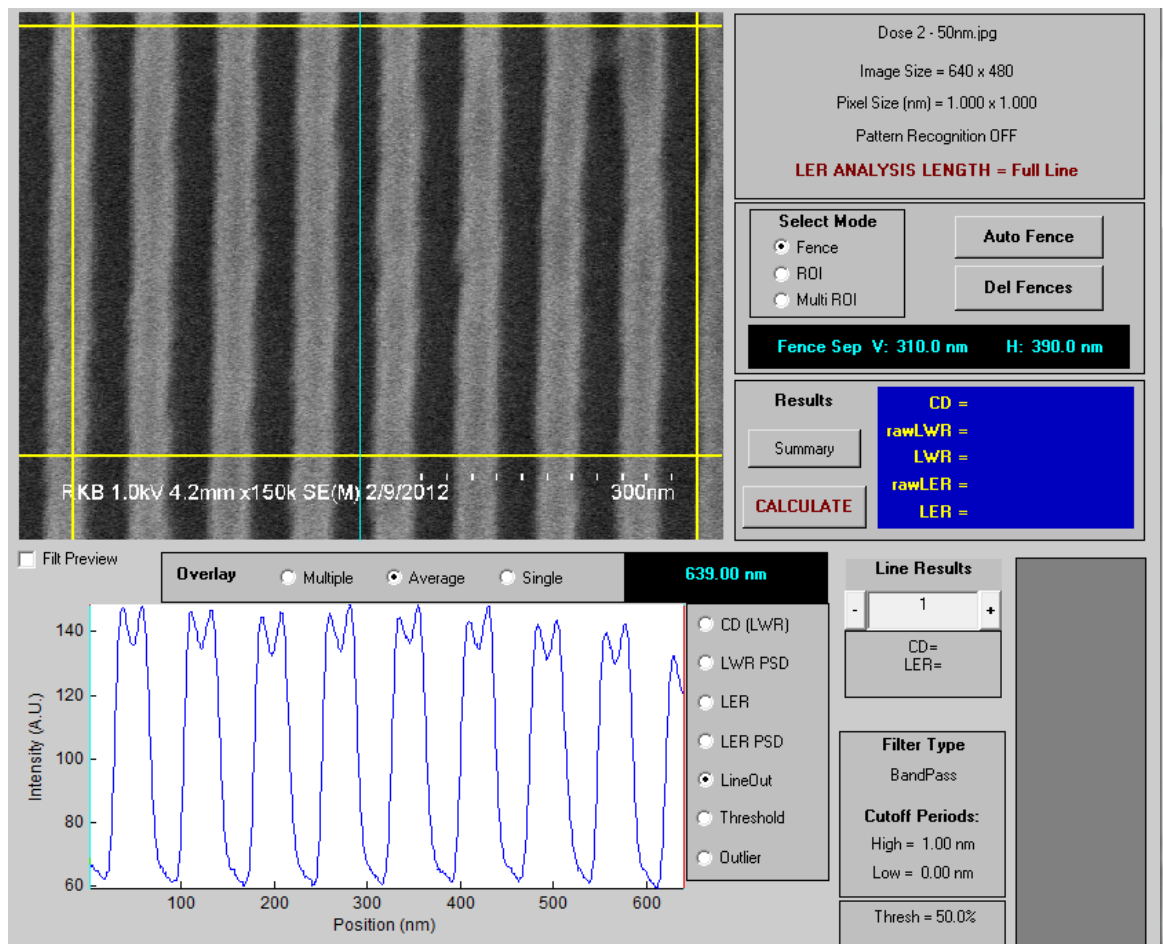


$$h(T) = w \left(\frac{M - G}{2} \right) \ln \left[\cosh \left(\frac{T - T_g}{w} \right) \right] + (T - T_g) \left(\frac{M + G}{2} \right) + c \quad (1)$$

Films were heated from 25 to 160 °C for 20 mins to outgas residual solvent. Measurements were then taken on cooling from 160 to 25 °C for 20 mins and data fitted to Dalnoki-Veress eq.

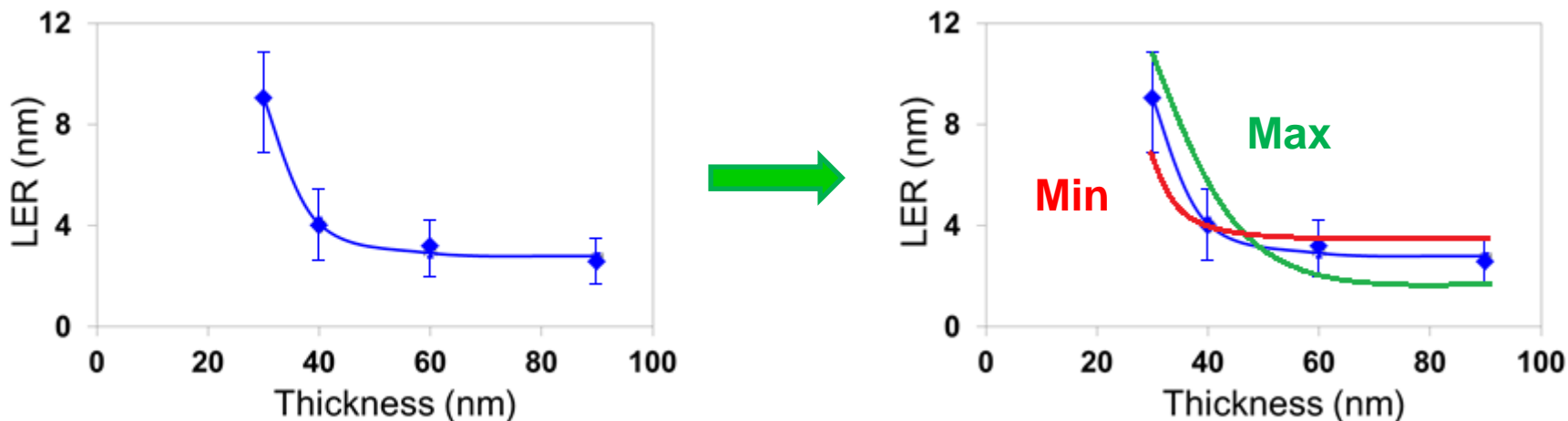
LER Measurements (BMET Data)

Summit V8.8.0



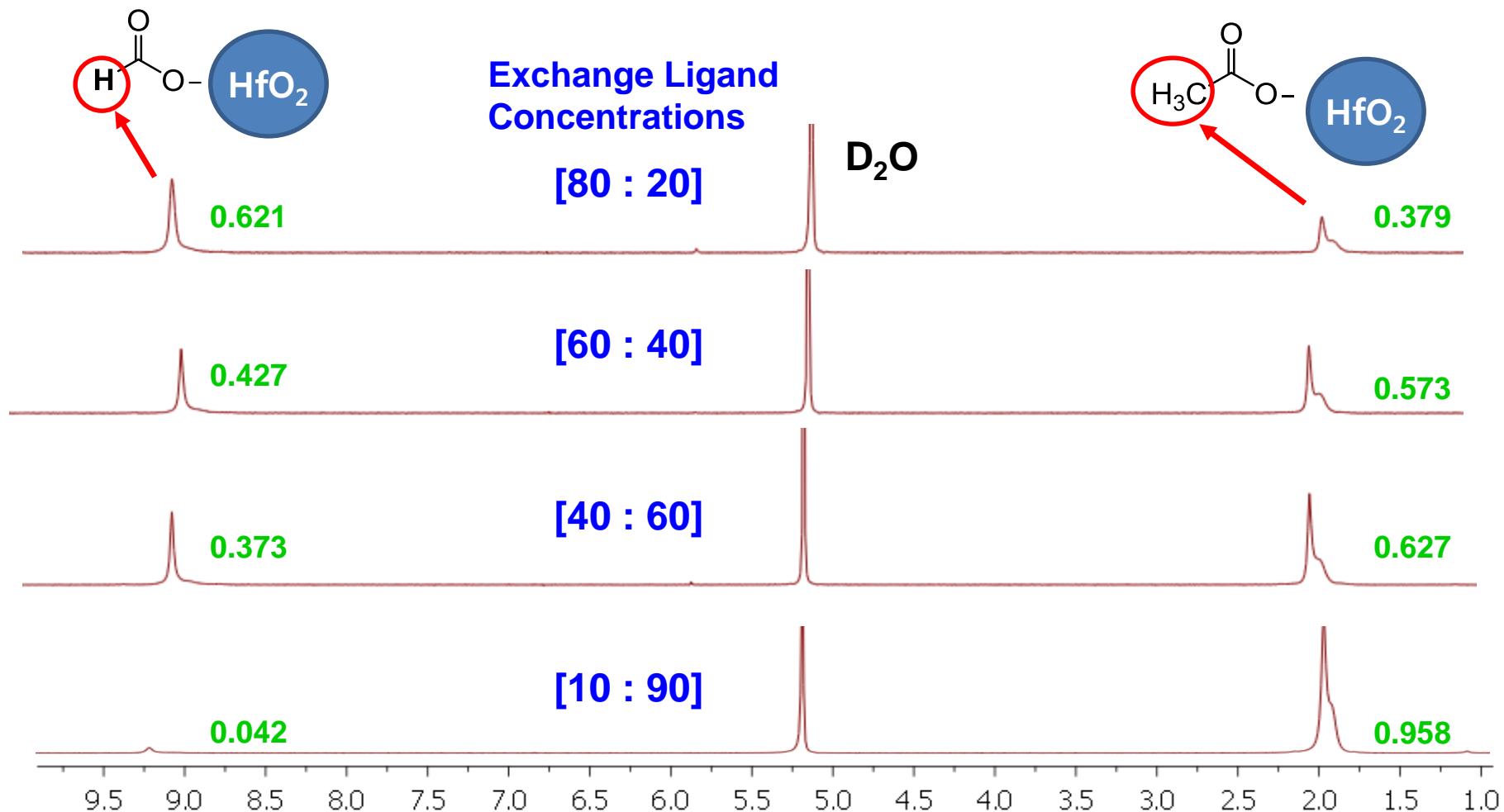
- 7 lines
- 580 nm length
- Threshold = 0.5
- Spatial Frequency from 1 to 400 μm^{-1}

Error Calculations



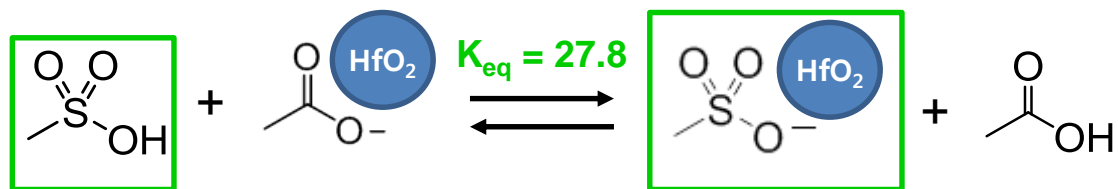
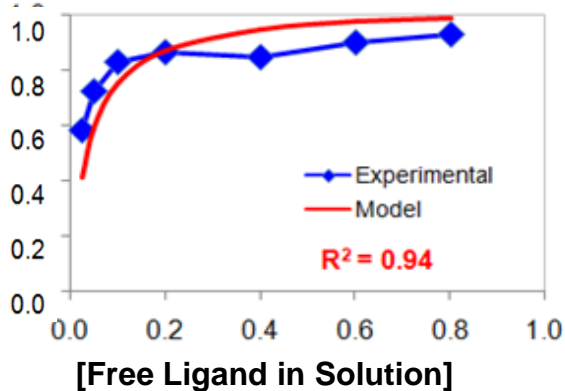
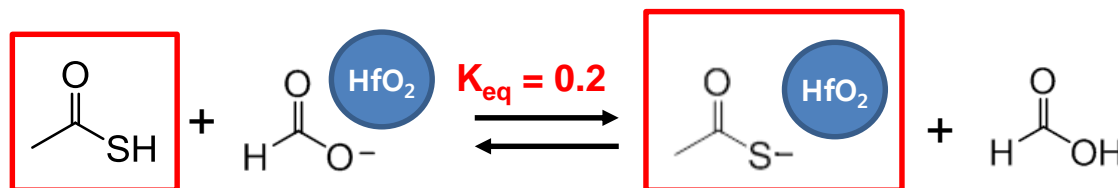
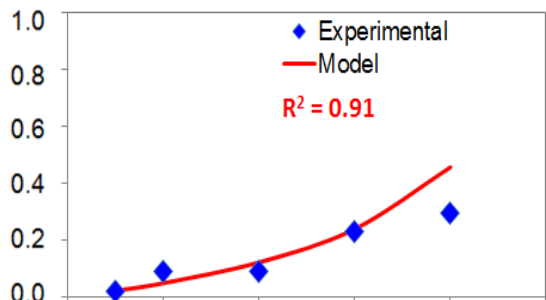
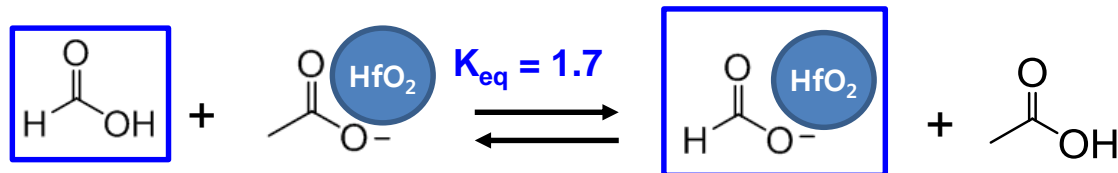
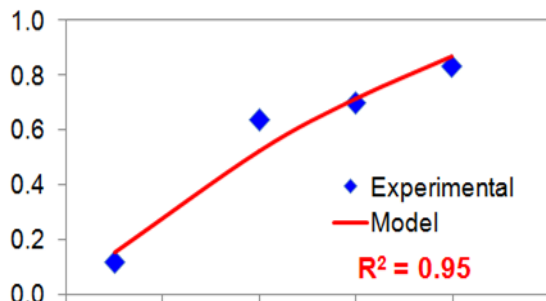
- For each curve, the individual point error was added to the LER at 30 and 40 nm thick while subtracted at the 60 and 90 nm thick to get the max data set.
- Subtracting the each error at 30 and 40 nm while adding the error at the 60 and 90 nm data gave the min error.
- The max and min error sets were then modeled and the areas determined.
- The difference between the max and min area was used as the error bars.

Nanoparticle Exchange / Precipitation



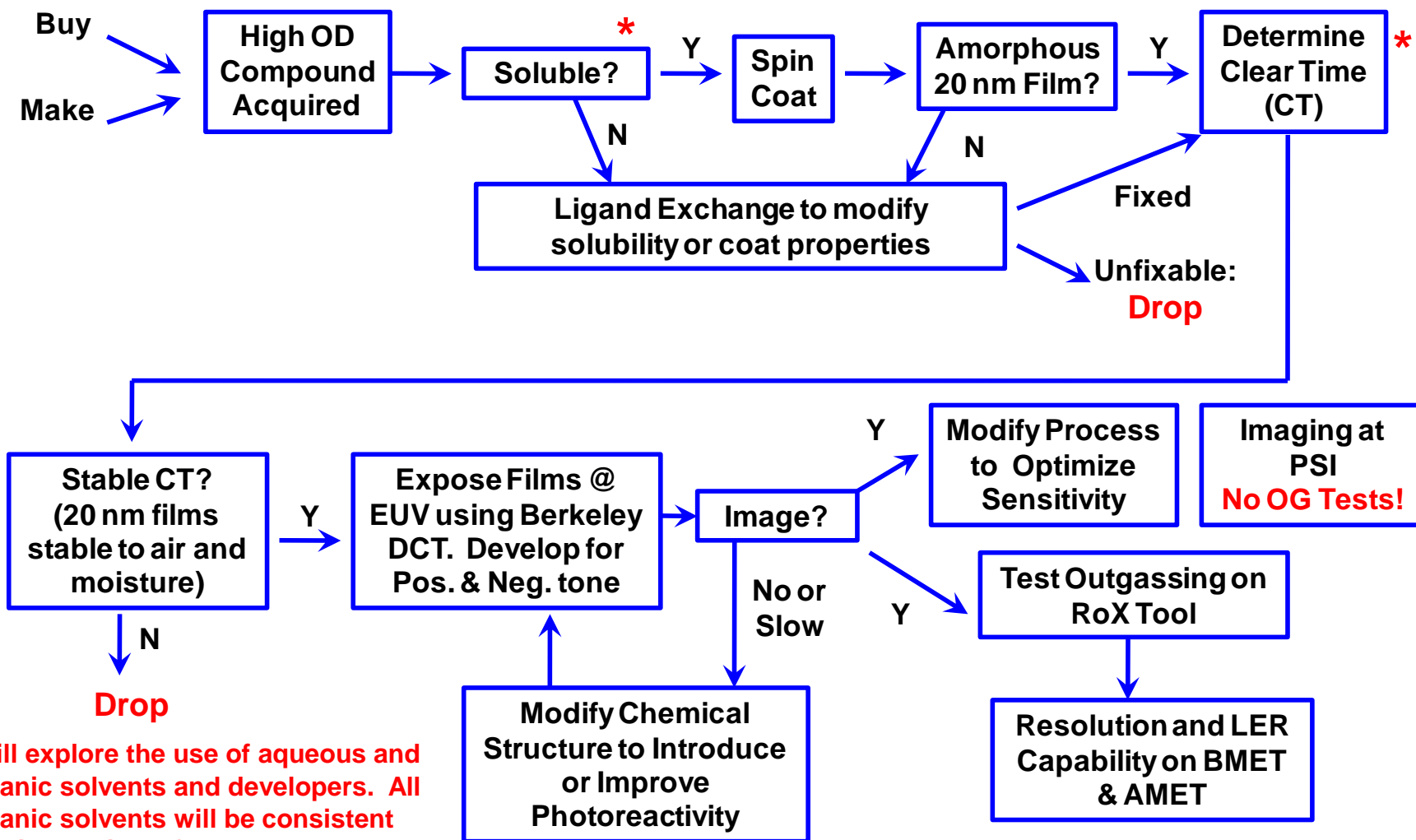
Thermodynamic Results for Ligand Binding

[Ligand Bound to Nanoparticle]



¥ - Related to acetic acid through the formate-acetate binding energy

We will rapidly determine which chemical families show the best promise for detailed study



***Will explore the use of aqueous and organic solvents and developers. All organic solvents will be consistent with industrial safety standards.**

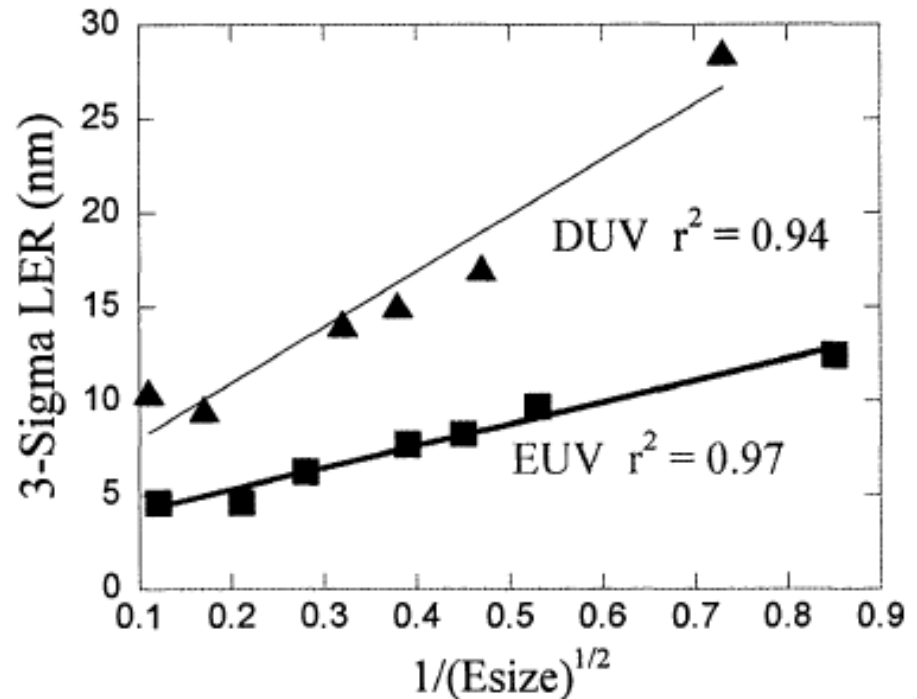
Shot Noise

Poisson Statistical Model:

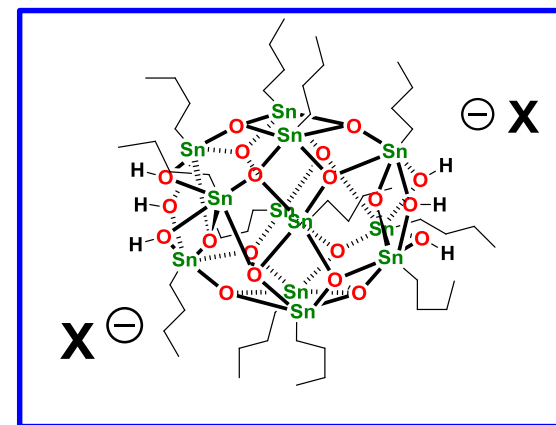
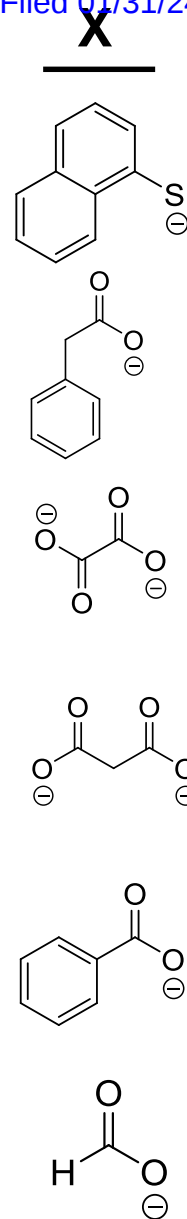
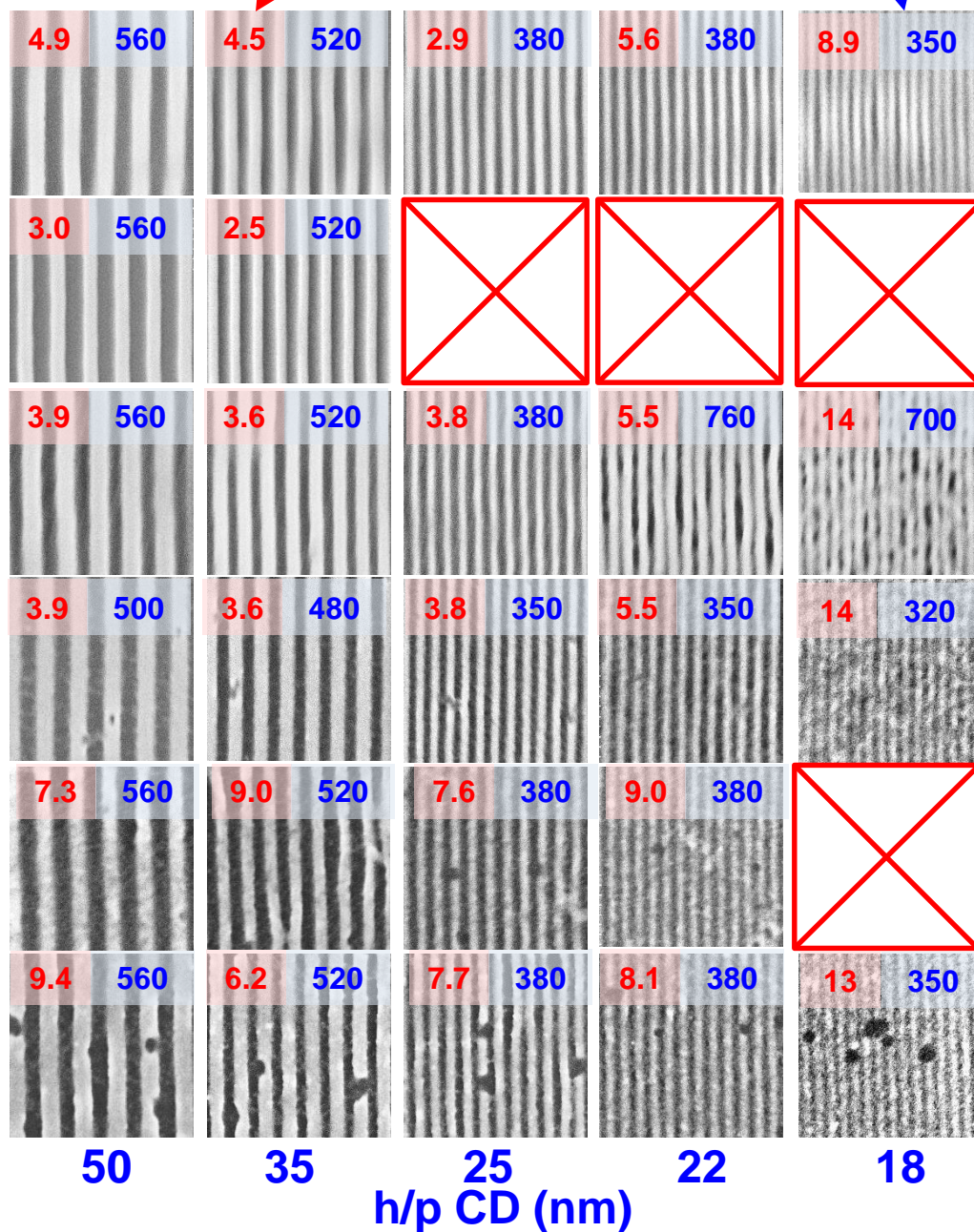
σ_N – Statistical Variation in Dose
 N – Number of Absorbed Photons

$$\sigma_N = \sqrt{N}$$

$$LER \propto \frac{\sigma_N}{N} = \frac{1}{\sqrt{N}} \propto \frac{1}{\sqrt{dose}}$$

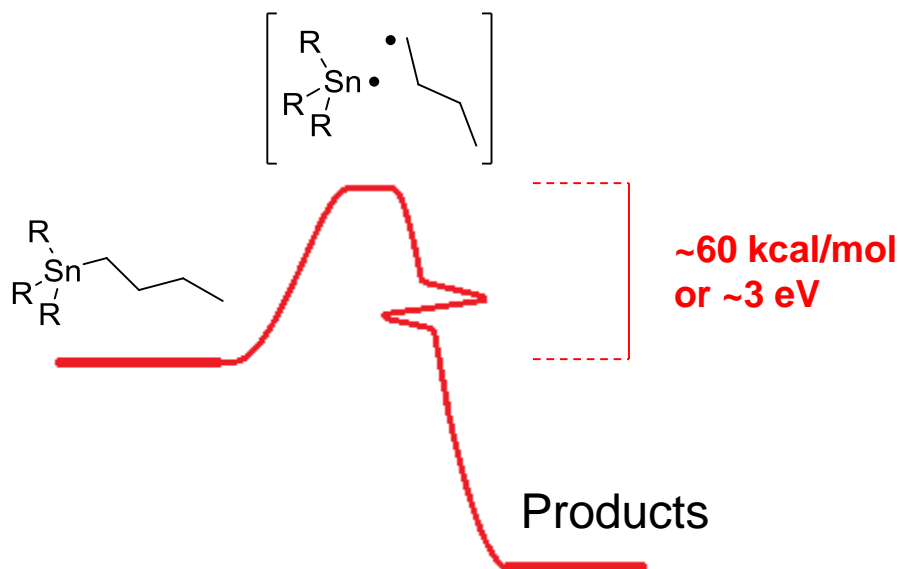


**As the number of absorbed photons increases, the LER decreases.
 If more photons are absorbed for any given material, LER should decrease.**



Correlation between ligand structure and sensitivity

Case 1:24-cv-00126-PKS-ML Document 24-05 Filed 04/31/24 Page 64 of 84



Decreasing the energy of the rate-limiting transition state should increase the probability of reaction (and thus the sensitivity)

